

# PREPARATION OF HIGH REFRACTIVE INDEX GLASS MICROSPHERES AND STUDY OF THEIR REFLEX-REFLECTIVE CHARACTERISTICS

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

BY  
KEWAL KRISHAN VERMA

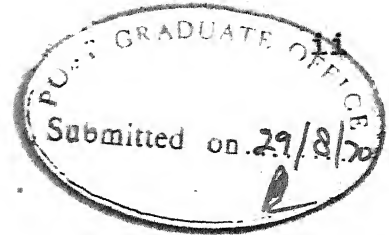
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DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
SEPTEMBER, 1970

CERTIFICATE



Certified that the work 'Preparation of High Refractive Index Glass Microspheres and Study of their Reflex-Reflective Characteristics' has been carried out under my supervision; and the same has not been submitted elsewhere for a degree.

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ABSTRACT

(The use of high refractive index glass spheres in reflex-reflecting surfaces have been popular since quite sometime. Such reflex-reflectors are used commonly for highway markings and road side signs. A typical reflex-reflecting surface essentially consists of a layer of glass spheres backed by a metallic reflective backing held in an underlying layer of a transparent binder material, and an overlying transparent coating covering the spheres.)

✓ High refractive index glass microspheres in the range 10-80 microns with refractive index greater than 2.1 were prepared in the system  $\text{PbO-TiO}_2\text{-BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$  and  $\text{ZnO}$ . Reflex-reflective characteristics of these glass spheres have been studied in two size ranges, 22 and 52 microns, coated on three different surfaces, namely, a buffed aluminum surface, a mirror surface and a non-reflecting black paper. ✓

(The buffed aluminum surface coated with glass spheres showed compareable results with a commercially reflex-reflecting sheet. Reflex-reflective characteristics of the glass spheres coated on a non-reflecting black paper showed evidence that our glass microspheres can also be used on any rough and non-reflecting surface and still sufficient reflex-reflection action can be seen.)



## 1. INTRODUCTION

High refractive index glass microspheres have been successfully used in making sphere lens optical elements of the type of reflex reflectors. The characteristic of such a reflector in returning back a brilliant cone of light toward the source of an angularly incident beam of light, gives rise to the term reflex-reflector. This characteristic distinguishes such reflectors from ordinary mirror which causes specular reflection and from diffusing types of reflectors which dissipate the incident light in all directions without selective return in the direction of incident light. Glass spheres, used in reflex reflector markings for highways, highway signs, curbing, railway lines and other like uses, reflect light with a glow, giving a 'luminescent' effect both during night and foggy days. It has been found that such markings not only increase visibility at night, but also, the presence of glass spheres markedly increases the life of the markings.

To be effective for such uses these glass micro-spheres must have certain special features. These should have fairly high refractive index, be transparent, weather resistant, abrasion resistant and chemically stable. Glass spheres, coated on reflex reflecting surfaces, having refractive index of about 1.6, in recent years have been replaced by spheres



with higher refractive index values. Refractive index of 2.0 or even higher have been employed.

In this research project a glass of refractive index greater than 2.1 has been prepared. The composition of glass has been carefully chosen considering its high refractive index, weather resistance and chemical stability requirements. More than twenty different compositions have been melted in recrystallised alumina and platinum crucibles, using heavy duty glow bar furnaces. The system finally decided to work on was  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$ .

In above system glass has been prepared by mixing the roughly powder oxides of analytical grade of Pb, Ti, Al, Ba, Zn and Boric acid for  $\text{B}_2\text{O}_3$  and melting in nonporous high alumina fireclay crucibles. Glass melt from  $1300^\circ\text{C}$  has been successfully cast in water cooled aluminum molds with an idea of avoiding devitrification of the glass composition and bubble formation which is likely in water quenching of the melt.

Wet grinding in a ceramic ball mill followed by wet sieving have been used to get fine glass powder in normal size range of -200 # and +400 # (ASTM Sieve numbers). Sedimentation techniques have been subsequently used to obtain two powder samples with average sizes as 26 micron and 62 micron respectively from the sieved range for spheroidisation of the glass powder.

The particles have been spheroidised by injecting in a uniformly flowing spray form, through an envelope of oxy-acetylene flame. The stream of molten glass particles have been found to take the spherical shape due to surface tension forces. The two glass powder samples have been spheroidised under standardised conditions of flow rates of oxygen and acetylene gases, feed rate of powder, flow rate of compressed air used to obtain a well dispersed flow of glass particles and the temperature conditions. These conditions have been standardised to give maximum spheroidisation.

The two samples of glass spheres thus obtained, having average sizes of 22 micron and 52 micron respectively, have been coated on three different surfaces, namely, a buffed aluminum surface, mirror surface and a non-reflecting black paper, for the study of their reflex-reflective characteristics.

A simple reflectivity apparatus for reflectivity measurements, consisting of a source of collimated light beam, a specimen holder mounted in the direction of incident light and a photocell has been designed. Microvolts generated by the reflected light from the coated reflex-reflective surface and falling on the photocell have been measured accurately across a standard resistance using a microvoltmeter. The angular dependence of these readings have been compared with a commercial reflex-reflective surface taken as a standard and efficiency of the surfaces coated with 22 and 52 micron

glass spheres have been compared with this standard reflector.

An important consideration which can be employed in evaluation of surfaces coated with glass spheres has been taken in this work. For better comparison of the reflex-reflective characteristics, a term absolute reflectivity has been defined. In this term the percent area occupied by the glass microspheres which are coated in a monolayer on the reflecting surface has been considered.

## 2. A BRIEF REVIEW OF THE PROBLEM

### 2.1 Reflex-Reflectors:

The use of spherical lenses<sup>1</sup> for reflex-reflection has been made since early 30's. Under the name of retro-directive reflectors. These were used to return light into the immediate neighborhood of its source, regardless of the position of that source. This requirement for the reflected light, in early period of the progress on such reflectors, was met using a combination of prisms, mirrors coupled with concavoconvex lenses, or a lense mirror plaque. A typical example can be a number of small lenses molded side by side on one surface of a single piece of glass, each lense having a silvered back, of a proper shape to accomplish the reflection. A practical example of such a reflector is the red coloured reflector used at the back of a bicycle which appears luminescent when light is made to fall on it.

In the latter and improved form of reflex-reflectors glass beads in the size range of 0.001 to 0.01 inch and with reasonably high refractive index of the order of 1.55-1.6 have been employed. A typical reflex-reflector using high refractive index glass consisted of a monolayer of small transparent sphere-lens elements (glass spheres), an underlying light-reflective layer or surface which is optically and physically

united to the back extremities of the lense elements, and an overlying transparent coating covering the layer of lens elements and having a flat front surface.<sup>2</sup>

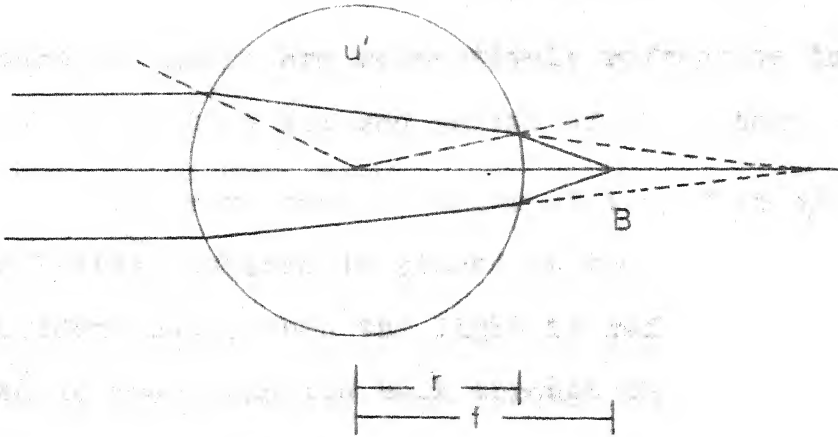
In the following years till 1967, reflex-reflector sheetings have been improved in terms of glass composition, binders for holding the glass spheres, transparent covering layer above the particles, light reflective layer underlying the spheres, techniques of coating of reflex-reflective sheets with glass spheres, techniques of laying underlying and covering layers on glass spheres and methods of production of the glass spheres. All these topics will be considered later, citing relevent references showing the sequential progress. But before starting these let us examine the importance of refractive index of these glass spheres and the underlying light reflective backing layer, by looking at the spherical lens optics<sup>3,4</sup> applied to the problem of reflex reflection.

In Fig. 1(a), schematically a simple optical system for a single glass sphere is shown. Incident light, due to the glass sphere placed in the path of light converges to a focal point B behind the sphere. The position of the focal point for a spherical lens is governed by refractive index of the particular glass. Assuming it to be a perfect sphere and considering an incident beam width small compared to the radius, in which case the optical center is coincident with the center of the sphere and applying geometric optics the

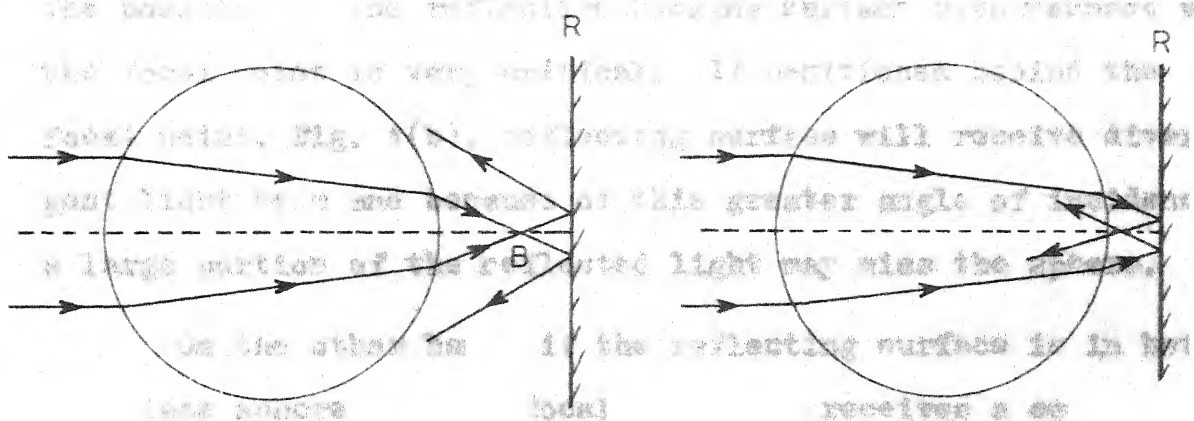
$u'$ , REFRACTIVE INDEX OF THE  
GLASS SPHERE

B, FOCUS

R, REFLECTING BACKING



(a)



(b)

(c)

FIG-1. DIGRAM SHOWING THE PATH OF A RAY OF  
LIGHT FALLING ON A GLASS SPHERE AND  
EFFECT OF POSITION OF REFLECTIVE BACKING



focal length measured from the center of the sphere is given by an expression,

$$f = \frac{u'r}{2(u'-1)}$$

where,  $u'$  and  $r$  are respectively refractive index of the glass with respect to air and radius of the sphere.

For a refractive index of 1.5,  $f$  is  $3/2$  times  $r$ . If a reflecting surface is placed at the focal point and normal to incident beam, then the light is reflected back into the sphere and is re-collimated back through the lens.

If a high degree of reflex-reflection is to be achieved, the position of the reflective backing surface with respect to the focal point is very critical. If positioned behind the focal point, Fig. 1(b), reflecting surface will receive divergent light beam and because of this greater angle of incidence, a large portion of the reflected light may miss the sphere.

On the other hand, if the reflecting surface is in between the glass sphere and the focal point, it receives a converging light beam and returns it through the sphere in a widely divergent cone. In this case a larger area of the surface is illuminated by the converging light which is reflected into the lens rather than away from it as was seen in the last case.

If, in the relation  $f = u'r/2(u'-1)$ , the refractive index of the glass sphere approaches 2.0,  $f$  approaches  $r$  and the focal point coincides with the trailing surface of the glass sphere.

For refractive index greater than 2.0, the focal point moves inside the sphere, which means that all the refraction is produced by the front surface only. New equation of the form,

$$f = \frac{r}{u'-1}$$

will be valid and here also for  $u' = 2$ ,  $f = r$ .

Fig. 2 shows a glass sphere embedded in a transparent medium backed by reflecting surfaces coinciding with the focus of the sphere. In the arrangement shown in Fig. 2(a) incident beam of light has to be perpendicular to the reflective backing surface for proper reflex-reflection action. However, in the arrangement for Fig. 2(b) where the reflecting surface is spherical one concentric with the sphere and coincident with the focal plane, incident light at any inclination can be properly returned.

The rear surface of a glass sphere will normally reflect a portion of the incident beam and transmit and absorb the remainder. A reflective backing will cut off the portion of the transmitted light and add to the intensity of the reflected beam. However, the amount of incident beam returned back will depend upon the position of the focus, the intensity being increased as the focus shifts into the sphere when refractive index of the glass exceeds the approximate value of 2.0.

Keeping these considerations in view the design of P.V. Palmquist<sup>2</sup> has been improved in the following years. In



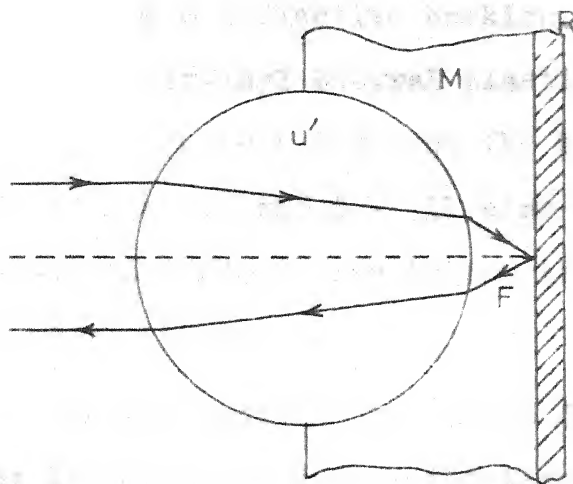


FIG. 2(a)

$u'$  REFRACTIVE INDEX OF  
GLASS SPHERE

F FOCUS

M. TRANSPARENT MEDIUM

R REFLECTIVE BACKING

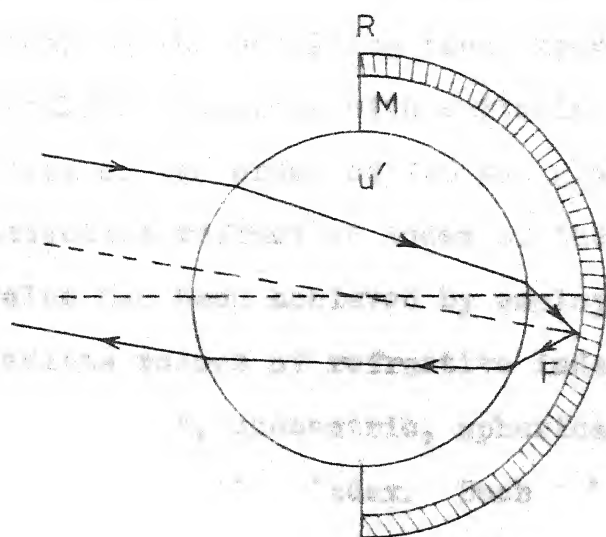


FIG. 2(b)

FIG. 2 SCHEMATIC ARRANGEMENT OF GLASS SPHERES EMBEDDED IN TRANSPARENT MEDIUM OVERLYING THE REFLECTIVE BACKING.

1951<sup>5</sup> a moldable layer containing aluminum flake pigment has been used as a reflective backing. The next layer is composed solely of polyvinyl butyral plastic and transparent pigment. On top of this is a layer of the binder. Transparent glass beads of  $n = 1.9$  and 5-7 mil size are applied to the coated and uncured binder. The latter is cured after the application of the beads.

An improvement over above design by N.W. Taylor<sup>6</sup> in order to secure maximum reflection brilliancy with this type of reflector, is the use of the effective refractive index of the sphere-lens elements of about 1.9 times the refractive index of the overlying transparent coating. Since commercially available coatings with suitable compositions had refractive index of the order of 1.5 the glass spheres used were of an effective refractive index of the order of 2.9. The latter value has been achieved by employing glass spheres, of intermediate values of refractive index, which are provided with a transparent, concentric, spherical, surface layer having a lower refractive index. Such spherical-lens elements of the composite sphere-lens type have been produced by forming a suitable porous surface layer around the core of the glass sphere by a chemical leaching treatment of the spheres. By this treatment a soluble component of the surface region is extracted and the leached surface layer of a glass sphere has a reduced refractive index because it is porous and is permeated by a substantial proportion by volume of air or of an

impregnant liquid or solid material of relatively low refractive index. The thickness of this layer is a minor fraction of the diameter of the core. The core and the surrounding layer of the glass sphere together serve as a composite two-element sphere-lens, with an effective refractive index greater than that of the glass sphere core. While preparing a reflex-reflective surface, the layer of such glass spheres has again an underlying concave reflective surface. The assembly brings the incident light to a focus at the reflective surface and maximum reflex-reflection brilliancy is secured both for normally incident light beams and for angularly incident light beams due to the concentric concave surface of the reflective layer associated with each sphere.

Another kind of glass microspheres to be used as suspension in transparent varnishes, paints or pigments have been suggested by P.V. Palmquist in 1960<sup>7</sup>. Such reflective varnish compositions can be readily formulated for application in various ways, as by spraying, painting, printing and screen-processing, to provide reflective coatings by a single-step procedure. The glass microspheres employed here have high refractive index, are transparent and reflectorized over approximately half its area, conveniently with a thin metallic reflector coating, such as a coating of aluminum forming an integral hemispherical reflector cap, the combination being reflex-reflecting. This hemispherical metallic coating provides a reflector both for light rays which penetrate the uncoated half of the microsphere and impinge upon the concave inner surface of the metal coating,

and for light rays which impinge upon the convex outer surface of the metal coating.

Very recent work done in the field of reflex-reflection has appeared in the form of patents in the year 1966<sup>8,9,10</sup>. In the first patent small retro-reflective particles have been used. These consist of a core of a cured, monolithic thermosetting material. The surface of the core is covered with small glass spheres. These are partially embedded and securely held on the surface. The high refractive index glass spheres have size in the range  $1/2 - 30$  mils. Whereas, the core has a diameter several times bigger than the glass spheres. These reflective spheroids are used in highway markers.

In the same year, Eduard R. De Vries suggested the use of a transparent binder material containing a sufficient number of cured reflectively colored abrasive resistant resin coated glass beads. These beads mixed with a colour pigment are added in the binder material. Uncoated glass beads of diameter in the range 10-50 mils are mixed with this. The whole mixture containing small coated beads, bigger uncoated beads and the binder form the reflective coating composition.

A still novel suggestion has been made by Samuel E. Wissinger, Jr.<sup>10</sup> He suggests the use of glass spheres in the range of 3-100 mils, which reflect light from within the sphere irrespective of the refractive index of the glass. The reflectorising glass spheres are produced from small glass spheres which

have been fractured and coated so as to yield spheres which hold together but which reflect light due to the fractures within the spheres. These fractures act like little facets for reflecting light in the same fashion as a cut diamond reflects light. The internal fractures in the glass spheres are obtained by producing internal stresses and strains by sudden change in temperature while simultaneously coating the spheres with a bonding agent. This is achieved by quenching the hot glass spheres, from temperature lower than the fusion point of glass into a cold bonding liquid.

## 2.2 High Refractive Index Glass Systems:

A very important and tricky consideration in this field is the choice of a suitable glass composition which can form a transparent glass with high refractive index added by weather resistance, abrasion resistance and chemical stability. Besides these considerations the glass should have a reasonably low fusion point and should have a low viscosity for free flow of the melt at temperatures slightly higher than the fusion point of the glass, this being very important in the manufacture of glass spheres since the molten particles of glass form themselves into spheres due to the surface tension effect.

From the personal experience on the laboratory scale and a brief literature survey it has been found that usually the glass elements used for the preparation of high refractive index microspheres form very corrosive melts. These glasses



in the molten state not only react with the container and corrode it but they themselves are very much susceptible to reaction with the furnace atmosphere.

Another problem that is commonly faced in the production of these glasses is their devitrification tendencies. Special techniques and care are required to cast such glass in molds or quench them into water. The latter is employed under many circumstances.

A certain glass forming composition may be chosen from the known glass forming systems<sup>11</sup> and further addition of elements can be made depending upon the special properties desired. Approximately how much of a certain element should be added in order to get a desired property like refractive index or density of the glass can be predicted, since both of these change as a function of the composition<sup>12</sup> to some extent. But, whether the particular system chosen will form a glass or not can be found out only after trying the composition in a suitable container and furnace.

Among the popular glass systems which have been used in making high refractive index microspheres for use in the reflex-reflectors<sup>core</sup> are examined below.

Refractive index of 2.1 to 2.5, along with chemical stability, stability to the sunlight and to exposure to humid atmosphere has been obtained in a glass system<sup>13</sup> using substantial proportion of bismuth oxide (10-65 percent) and a high content of

titanium oxide (20-50 percent). These can be used without other oxides, or may preferably include one or more of the following: lead oxide, barium oxide, zinc oxide, cadmium oxide and boron oxide. Basically the system can be designated as  $TiO_2$ - $Bi_2O_3$ - $PbO$ - $BaO$  type.

Another simple system consisted of two components only,  $TiO_2$  and  $PbO$ <sup>14</sup>. By keeping titanium oxide within the range of 15 to 50 weight percent and lead oxide within the range of 85 to 50 weight percent, high refractive index of 2.4 was achieved. Also transparency and resistance to weathering required of small glass microspheres as in reflex reflectors, was attainable.

A number of glasses with refractive index of at least 2.1 and with other desired properties, have been prepared using oxides of metal which are not the usual kind of glass forming oxides<sup>15</sup>. These are the oxides of metals, bismuth, lead, thallium, tungsten, tantalum and cadmium. These oxides are not glass formers nor are they capable of imparting glass forming ability to compositions which do not contain one or more recognised glass forming ingredients of the type  $B_2O_3$ ,  $SiO_2$ ,  $P_2O_5$  and  $GeO_2$ . However, they have the property of forming glasses, when used in combination together, which may also have less devitrification tendencies.

In the system  $TiO_2$ - $BaO$ - $B_2O_3$ - $ZnO$ <sup>16</sup>, glasses with refractive index of the order of 1.9 and above, having all other desired properties have been prepared. Special characteristic

of these glasses have been their water white colour and absence of oxides of silicon and lead.

Another simple system, comprising  $\text{BaO-TiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ <sup>17</sup> has been used to obtain glass with a refractive index of the order of 1.9 along with other desired properties.

In recent years use of larger fractions of  $\text{TiO}_2$  have been frequently made to obtain glasses for the manufacture of high refractive index glass microspheres. Among these is a system<sup>18</sup>  $\text{TiO}_2\text{-67.5}$ ,  $\text{CaO-10}$ ,  $\text{BaO-15.2}$ ,  $\text{Bi}_2\text{O}_3\text{-5}$ ,  $\text{SiO}_2\text{-2.0}$  and  $\text{B}_2\text{O}_3\text{-0.3}$  weight percent, which has an extra high refractive index of about 2.1.

For use as reflective beads in highway marking paints and road side signs, in a very recent invention high alkali earth oxides<sup>19</sup> have been used. These glass bead compositions include lime, silica or titanium oxide and a flux such as borax or boric acid, or other substitutions in whole or in part of magnesium, barium or strontium oxides for the lime. The important characteristic of such a system is the low cost of production of glass, and its low viscosity which is of great advantage in the manufacture of truly spherical glass beads. Glasses of refractive index 1.6-1.9 can be prepared by substituting silica with larger quantities of rutile form of  $\text{TiO}_2$  and a higher refractive index alkali earth oxide as  $\text{BaO}$ .



## 2.3 Production of Glass Spheres:

Various methods<sup>20-24</sup> have been employed for the production of glass spheres of desired size. Among these according to one suitable method<sup>20</sup>, small glass particles are blown or dropped into a body of air or inert gas which has been heated to a temperature well above the fusion point of the glass. These particles melt at the suitable temperature and take a spherical shape by the effect of surface tension. They subsequently enter a cold zone where they solidify into transparent glass spheres without devitrification. Another method used for forming them involves preliminary heating of a suitable glass to a molten condition, and then breaking it up into minute globules by the application of a jet of high velocity gas. The particles in the molten condition are allowed to solidify while in suspension.

Among the above mentioned methods, the last one seems to be more flexible in terms of the production of glass spheres of different size. Controlling the temperature of the glass melt, size of nozzle through which the jet of high speed gas is injected and the velocity of jet, glass spheres of different size can be obtained. But in the first method only small glass spheres and of a closer size range can be produced. Such attempts to produce nearly uniform, larger sizes of glass spheres have been unsatisfactory because small particles of ground glass, can not be subjected to uniform heat or to a uniform period of treatment. When dropped through a zone of flame or a heat radiant source,

all the particles do not remain in the heat zone for a sufficient length of time to become properly or uniformly softened to be converted into spheres. Therefore, the yield of spherical bodies is only a small percentage of the total amount of ground glass particles dropped or projected through the flame.

In another method, glass spheres of relatively large size, about 6 mm., are prepared from preformed glass rod or tubing which is fed into a prescribed pattern of several burner flames. Droplets of the glass are separated from the main body of the solidified glass by heating an end of the rod or tube and allowing each droplet to separate by gravity upon its being heat-softened by the burner fires. Producing glass spheres this way requires that the glass be first fabricated into rod, or tubing suitable for feeding into glass sphere-making furnace. Another limitation of the method is the size of the bead produced irrespective of the diameter of the rod or tube.

In an improved form of above method,<sup>21</sup> using a molten supply source, a downwardly flowing stream of molten glass, emits from an orifice of controlled dimensions. The stream of glass discharging from the orifice is intercepted by a pattern of burner jets capable of separating the stream into small droplets of molten glass. These charges are then conveyed into a rotating cylinder or kiln which serves to finally shape the respective charges of glass into spherical form.

A very recent design of a glass bead making furnace has been suggested by Elmer L. Schmidt<sup>24</sup>. In this method glass beads are formed from ground glass, which is subjected to high temperature in a vertical furnace tube. In the furnace tube the glass is charged with the combustion gas in such a manner that the glass particles are caused to be discharged upwardly with the burner flame into the furnace. Combustion gas is mixed with the air and charged into the burner where the gases are burnt to produce a hot flame which is directed upwards and through the entire extent of the furnace tube to provide heating. The glass particles, passing through the burner and into the flame, melt and take spherical shape because of surface tension effect.

Special feature of this design is a provision for admitting air under pressure through the interior of the furnace around the walls to provide an upwardly rising air cushion. The swirling cushion of air provides protection in cooling for the furnace walls and also provide a barrier for the glass particles. Thus, the particles do not come in contact with the inner sides of the furnace walls and they tend to remain in the center region of the furnace as they pass upward. This reduces the possibility of deformation or malformations in the spheroidised glass particles, that might be caused by the physical contact of the glass spheres with the inner walls. The air cushion along the inner walls of the furnace, as a result of cooling the inner walls offers resistance to the formation of glass slag or other glass accretions to the interior of the furnace walls.

### 3. EXPERIMENTAL TECHNIQUES

#### 3.1 Preparation of Raw Materials:

Glass for the preparation of high refractive index microspheres was prepared in the system  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{ZnO}$ . Weighed quantities of analytic grade oxides of the metals Pb, Ti, Ba, Al and Zn and boric acid for  $\text{B}_2\text{O}_3$  were thoroughly mixed in a ceramic ball mill using water. After this simultaneous grinding and mixing of the powders for several hours, it was dried and melted in nonporous, high-alumina, fireclay crucibles.

About one kilogram of glass was prepared in batches of 50-100 gms. each. Glass was melted in a vertical glow bar furnace in which the crucibles could be introduced from the bottom.

From  $1300^\circ\text{C}$  the glass melt was quickly poured in a water cooled aluminum mold. Each batch of glass composition was slowly heated to  $200^\circ\text{C}$  followed by a very careful and slow heating from  $500\text{-}700^\circ\text{C}$ . From  $700^\circ\text{C}$  to  $1000^\circ\text{C}$  the heating rate was increased followed by another cycle of slow heating from  $1000\text{-}1300^\circ\text{C}$ . In all about 20 hrs. were spent for each batch of glass composition.

Glass thus produced was crushed in a ceramic mortar followed by wet grinding in a ceramic ball mill using water.

Mechanical grinding to get finely divided glass powder and separation of the powder in desired size fractions were simultaneously done.

Ground powder, for a small interval of time, was passed through a series of three sieves namely 120 #, 200 # and 400 # ASTM. By wet sieving, the glass powder was collected above 120 # and was again ground to get more fines followed by another cycle of wet sieving. The two fractions -120 # and +200 #, and -200 # and +400 # were dried and collected separately. The former was ground again in the ceramic ball mill, after almost all the +120 # glass powder had been ground, to obtain powder in the useful, -200 # and +400 #, size range.

Using standardised sedimentation technique, -200 # and +400 # glass powder was further separated into two size fractions, Sample -A and Sample -B. The former contained glass particles below 40 microns and the latter above 40 microns.

### 3.2 Spheroidisation of Glass Powder:

#### 3.2.1 Microsphere making furnace:

The schematic sketch of this furnace has been shown in Fig. 3. It mainly consists of a flame spray pistol, a special design by Shori Process Corporation, Par Washington, L.I., New York, which was used to make oxy-acetylene flame to provide high temperature zone for melting glass particles. It has a provision for feeding a fine dispersion of glass powder suspended in air, or oxygen, under pressure, through the

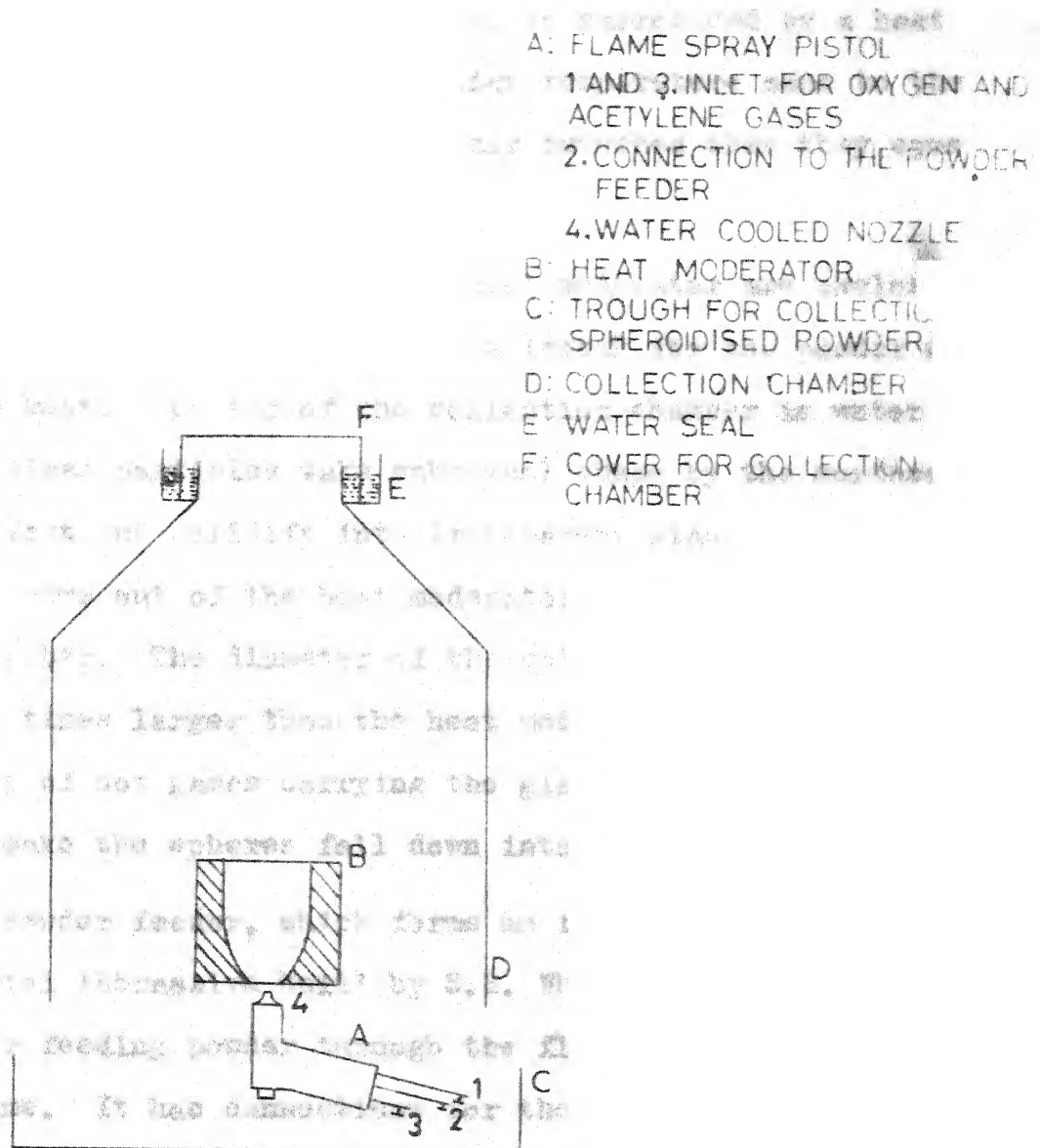


FIG. 3 A SCHEMATIC SKETCH OF THE EXPERIMENTAL SET UP USED FOR SPHEROIDISING POWDER



envelope of oxy-acetylene flame. An attachment for water cooling the nozzle has also been provided.

The flame from spray pistol is surrounded by a heat moderator to provide a uniform high temperature zone to the glass particles before they are air quenched when they come out of this zone.

The spray pistol and the heat moderator are enclosed in a collection chamber below which a trough for the powder collection is kept. The top of the collection chamber is water sealed. Molten glass particles take spherical shape by the surface tension effect and solidify into transparent glass micro-spheres as they come out of the heat moderator and enter into the collection chamber. The diameter of the collection chamber is kept several times larger than the heat moderator, to slow down the velocity of hot gases carrying the glass spheres appreciably and to make the spheres fall down into the trough.

Powder feeder, which forms an integral part of 'S.S. White Industrial Abrasive Unit' by S.S. White Mfg. Co., U.S.A., is used for feeding powder through the flame spray pistol and into the flame. It has connections for the compressed air supply and provision for controlling the powder feed by regulating pressure of the compressed air and vibrations of the powder container.

Provision is made to measure the flow rates of oxygen and acetylene gases and the compressed air by providing flow meters at the suitable places in this set-up for spheriodisation of glass powder.

### 3.2.2 Spheroidisation:

The two glass powder samples were spheroidised separately under conditions standardised for the maximum spheroidisation and the corresponding powder feeding rate, flow of oxygen, acetylene and air, and the temperature profile in heat moderator were recorded.

In order to keep the collection chamber cool, to facilitate air quenching of molten glass spheres in the collection chamber, water was constantly sprinkled on the outside walls of the chamber.

Spheroidised glass powder, collected in the trough for powder collection, was successfully obtained by removing water from the trough after the glass spheres had settled at the bottom and sweeping them with a brush after the powder had dried.

The glass powder samples, spheroidised for the conditions of maximum spheroidisation, were washed, thoroughly dried and rolled on an vibrating buffed aluminum sheet to remove the dirt and refractory chunks picked up by the powder during spheroidisation and the few glass particles still left as unspheroidised. These two samples which had almost complete spheroidisation the one with glass spheres below 40 microns was designated as Sample-C and one with spheres above 40 microns as Sample-D.

Actual feed rate of the glass powder into the flame was measured by collecting powder in a beaker, kept in front of the



flame spray pistol for a known time and weighing the collected amount. This was done under the same conditions at which the glass powder was spheroidised.

Temperature conditions for spheroidisation for the two samples were recorded by suspending a thermocouple in the high temperature zone. Oxy-acetylene flame formation and the air supply was kept the same as done during spheroidisation runs. The temperature was recorded at a number of points along the axis. One set of transverse reading was also taken from a fixed point on the axis.

### 3.3 Size Characterisation:

Microscopic techniques have been used for size characterisation of the unspheroidised as well as the spheroidised glass powder samples. Representative samples of the powder were prepared on glass microslides. The well dispersed glass particles on the slide were viewed under microscope at a suitable magnification and size of the particle was recorded by using a calibrated eye piece. A glass graticule on which a distance of one centimeter divided into hundred equal divisions was used in the eye piece of the microscope for the measurement.

After selecting a proper field of view, intercepts made by a reasonably large number of particles on the scale of the graticule were recorded. For a sufficiently large number of particles such intercepts give a fairly good size distribution of the particles. For unspheroidised material intercepts were noted and for spheroidised particles the actual diameters were used.

Besides careful examination of the transparency and homogeneity of the glass and the powder samples, density and refractive index of the latter were determined.

For density measurements of the glass spheres as well as unspheroidised glass particles the standard specific gravity bottle method was used. For weighing glass powder and liquid together in the bottle air bubbles were carefully removed by treating the sample in a vacuum desiccator.

Refractive index of the glass powder samples has been measured using standard liquids of known refractive index by the Beckeline method<sup>26</sup>.

### 3.5 Study of Reflex-Reflective Characteristics of the Glass Microspheres:

#### 3.5.1 Reflectivity apparatus:

A simple apparatus for the measurement of angular distribution of the reflected light from the surface coated with glass micro-spheres have been designed. As shown in Fig. 4, it consists of a base on which a source of collimated beam of light is provided. In front of this source there are two concentric discs capable of rotating independent of each other. On the center of the smaller disc, a specimen holder has been fixed. By rotating this disc, plane of the specimen can be rotated at a desired angle with respect to the direction of incident beam of light.

- A: SPECIMEN
- B: PHOTOCELL
- C: COLLIMATED LIGHT SURFACE
- $\theta_1$ : ANGLE BETWEEN THE DIRECTION OF INCIDENT LIGHT AND NORMAL TO THE PHOTOCELL
- $\theta_2$ : ANGLE BETWEEN THE DIRECTION OF INCIDENT LIGHT AND NORMAL TO THE SPECIMEN

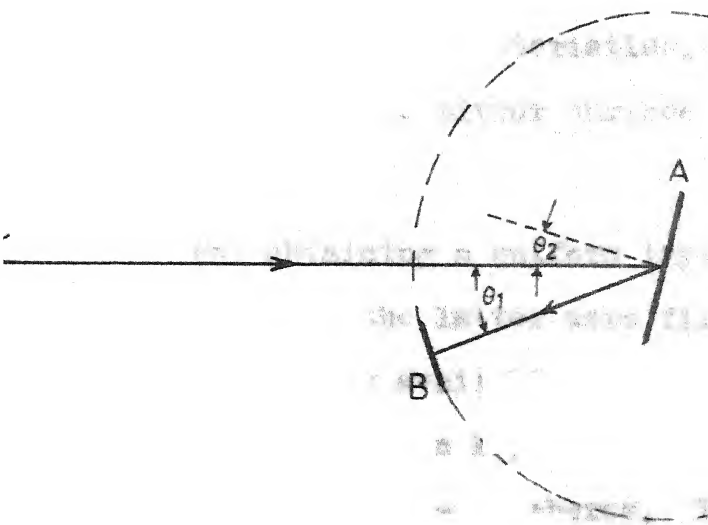


FIG. 4 SCHEMATIC REPRESENTATION OF THE REFLECTIVITY APPARATUS USED FOR STUDYING REFLEX-REFLECTIVE CHARACTERISTICS OF SURFACES COATED WITH GLASS SPHERES.

The bigger disc, kept below the smaller one containing the specimen holder, has a photocell holder fixed near its circumference such that when it is rotated at any angle with respect to the direction of incident beam of light the photocell always remains at the same distance from the specimen.

The photocell can be connected to any instrument capable of reading micro-amperes or micro-volts.

A cover for this whole assembly has been provided. The cover and the base of the reflectivity apparatus have been coated black to prevent internal reflection and external light.

### 3.5.2 Reflectivity measurements:

Three types of samples were prepared for the study of reflex-reflective characteristics, namely a buffed aluminum surface, a silvered mirror surface and a non reflecting black paper.

For obtaining a uniform layer of glass microspheres on these surfaces, the latter were first covered with a thin layer of a commercially available transparent binder material, in liquid form, and then kept under a well dispersed and uniform downward spray of glass spheres. Time of spray for obtaining a monolayer of spheres of almost uniform density was standardised by trial.

Using the same methods the three types of surfaces were coated with the glass microspheres of Sample-C and Sample -D.

Reflectivity measurements were taken on these coated surfaces using different orientations of the coated surface with respect to the direction of the incident beam of light and for each of these positions a set of readings on both the sides of the axis of incident beam of light were recorded. Stabilised voltage source was used for the collimated beam of light and the supply was carefully controlled to get the same intensity of the incident beam for every set of readings. For any arrangement of the sample the photocell was always kept normal to the reflected beam. Current generated in the photocell was read across a standard resistor connected with a microvoltmeter. The angular intensity distribution of the reflected light from coated surfaces was recorded as Percent Reflectivity against the angle made by the normal to the photocell with the direction of incident beam of light. Percent Reflectivity,  $R$ , has been defined as,

$$R = \frac{I}{I_0} \times 100$$

where  $I$  is the intensity of the reflected light from the specimen,  $I_0$  is the intensity of the incident light, both values have been recorded as microvolts.

For each of the reflective surfaces percent area occupied by the glass spheres was calculated by counting the number of spheres in an area of  $(1/40)^2 \text{ cm}^2$  as estimated from the calibrated graticule. The eye piece of the microscope in which

the graticule was placed had a magnification of 10X and the objective 40X.

Some glass spheres look darker because of the dirt and impurities picked up during melting of the glass and the spheroidisation process. These were examined under different conditions of illumination. It was achieved by looking at the glass spheres under different magnifications and thus the percentage of the spheres that appeared brighter were noted.

For the evaluation of the efficiency of the reflex-reflective surfaces a commercial reflex-reflective sheet was taken as a standard. Percent area occupied by the glass sphere and percent bright particles under different conditions of illumination were also determined for the commercial reflex-reflective sheet and the results were compared.

### 3.6 Representative Photomicrographs of the Glass Powder Samples:

A photographic record of the glass powder, the spheroidised as well as the unspheroidised, samples were also taken at suitable magnification.



## 4. EXPERIMENTAL RESULTS

### 4.1 Preparation of Glass and Powder Samples:

The glass melt was found to be very corrosive for the containers in which it was melted. Only one composition could be melted in one crucible. Although the glass melted in small platinum crucibles had shown a slightly yellow tinge, the glass formed in nonporous, fireclay crucibles picked up an amber colour.

Even in a slightly reducing atmosphere the glass formation was hindered and a nontransparent devitrified structure with purple coloration was formed. The same purple coloration was observed when larger amount of  $TiO_2$  was tried in the glass composition.

Glass system showed devitrification tendencies and therefore a rapid cooling rate was required. It could be successfully formed by pouring glass melt in water cooled aluminum molds. Although devitrification was thus avoided but sometimes a very thin layer of slag formation on the surface of the glass which was otherwise transparent and homogeneous.

The sedimentation scheme standardised for a column of about 30 cms. height and 500 cc capacity, to separate glass particles into two fractions containing particles below 40 microns, Sample -A, and containing above 40 microns, Sample -B, was as follows.

About 50 gms of -200 # and 400 # glass powder was taken in a 500 cc glass jar filled with water upto its capacity. It was found that the settling time for different size fractions could be determined by trial. After vigorously shaking the jar glass powder was allowed to settle for half an hour and then keeping the settled glass powder at the bottom, water from the top was decanted. The column was filled again with water and this time after shaking vigorously powder was allowed to settle for one minute only. After one minute the suspension containing glass particles mostly below 40 microns was transferred in a separate container. This process was repeated five times and for the sixth time the settling time was increased to two minutes. This time the glass particles left at the bottom of the column were above 40 microns. Particles below 40 microns removed repeatedly in the top suspension of the column were obtained from the suspension after allowing it to settle in a separate container for about 10 minutes.

#### 4.2 Spheroidisation of Glass Powder:

##### 4.2.1 Spheroidisation:

In both of the spheroidised samples C and D, the particles were mostly spherical and transparent. The coarser Sample-D had almost hundred percent spheres below 230 # (62 microns). A small fraction about 5 percent in the size range above 230 # remained unspheroidised. Bubbles were observed in both Sample-C and D. In the Sample -C they were less frequent and were observed

in 26 percent of the spheres where as in Sample -D they were observed in 80 percent of the spheres. The sizes of the bubbles were however larger in Sample-C and were of the order of a good fraction of the size of the sphere. Bubbles in sample B were fine and mostly around 2 microns and below.

#### 4.2.2 Conditions for spheroidisation:

Conditions for maximum spheroidisation have been tabulated in Table -1, in Appendix-A.

The temperature profile for the hot zone for two different standardised conditions of spheroidisation are shown in Fig. 5. Condition 1 was used for obtaining sample -C and condition 2 was used for obtaining Sample -D.

#### 4.3 Size Characterisation:

Results of size characterisation of Samples -A,B,C and D have been tabulated separately in Appendix -A, in Tables 2 to 5. Graphical representation of the size distribution has been shown in Figs. 6 and 7.

The average sizes of the glass particles in Samples -A,B, C and D, considering frequency of occurrence of a certain size in number percent, have been found to be 26, 62, 22 and 52 microns respectively.

#### 4.4 Physical Characteristics:

Massive glass in the system  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$  and ZnO prepared in nonporous fire clay crucibles has a light amber

colour, but it is transparent and homogeneous. When powdered they appear slightly lighter to the naked eye.

Density of the Samples -A and B was 4.49 g/cc. whereas, the spheroidised samples C and D had densities of 3.99 g/cc. and 4.23 g/cc. respectively.

Refractive indices of the unspheroidised powder and both of the spheroidised powders are above 2.1.

#### 4.5 Reflex-Reflective Characteristics:

##### 4.5.1 Sample preparation:

As compared to the standard commercially available reflex-reflecting sheet the prepared surfaces have a plane reflective backing as against the reflective backing forming a concentric cap at the back of the spheres in the former. The prepared samples also do not have the transparent covering layer overlying the layer of glass spheres. The glass spheres used on the commercial reflex-reflective sheet may be coated e.g. silicon coated beads<sup>31</sup>, for the ease in handling the glass spheres whereas our glass spheres did not have any such coating.

Visual inspection of the prepared reflex-reflecting surface and the commercial reflex-reflecting sheet by sticking them side by side on a wall in a dark room and shining light on them showed comparable results as far as the brightness of the surface is concerned. The 22 micron glass spheres coated on the buffed aluminum surface even looked brighter than the commercial reflecting sheet under the same conditions of illumination and inclination of the incident light.

#### 4.5.2 Reflectivity measurements:

Results of the reflectivity measurements on the surfaces coated with glass microspheres and blank surfaces have been recorded in tabulated form in Tables -6(a) to 6(i) and graphic form in Figs. 8 to 16. Table -7 and Table -8 respectively show the area occupied by the glass spheres on the coated surfaces and percent bright particles at different conditions of illumination.

In Table -9, reflex-reflective characteristics of 52 microns glass spheres have been recorded in terms of Absolute Reflectivity defined as,

$$\text{Absolute Reflectivity} = \frac{\text{Percent Reflectivity}}{(\text{fractional area covered by spheres}) \times (\text{fraction of bright spheres})}$$

The fraction bright spheres were counted at 50X which has been taken as condition for minimum illumination, as seen in Table -8.

Table -10 shows the evaluation of the efficiency of the coated surfaces as compared with the commercial reflex-reflecting sheet taken as a standard.

#### 4.6 Photomicrographs:

Representative pictures of the unspheroidised glass powder and the spheroidised ones have been shown in Appendix -A. Table-11 gives the description of these pictures and the magnification of the glass particles on these pictures.



## 5. DISCUSSION OF THE RESULTS

### 5.1 Glass Composition:

Choice of the final glass composition has been based on the properties desired of the glass spheres to be used in the reflex-reflectors.  $\text{PbO}$ ,  $\text{TiO}_2$  and  $\text{BaO}$  additions in the glass system increases the refractive index.  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  are added to impart weather resistant properties to the glass spheres.  $\text{ZnO}$  serves a dual purpose in that it increases the refractive index and at the same time acts as a bleacher of colour. Addition of  $\text{TiO}_2$  for increasing the refractive index needed a careful consideration because it also increases the devitrification tendencies of the glass melt and makes it more sensitive to the atmosphere in the furnace, used for melting glass. In a reducing atmosphere, for example if the crucible containing glass composition is heated in a silicon element furnace, close to the heating element and without proper shielding, a devitrified glass with purple coloration is formed. However,  $\text{B}_2\text{O}_3$ , which is a glass former too, in addition with  $\text{PbO}$  increases the vitreousity, homogeneity and fluidity of the glass composition. Our glass system  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{ZnO}$  has all these properties.

### 5.2 Glass Melting:

Each batch melting of the glass took about 20 hours, and only one batch could be melted in one crucible. These crucibles were of special composition and were slip cast in the laboratory.



This glass had to be melted in impervious containers due to its high fluidity and corrosive nature or else it penetrated into the pores and reacted with the crucible.

These slip cast, nonporous, high alumina, fireclay crucibles were to be heated very carefully at a slow rate. Slow heating rate at higher temperature range of 1000-1300°C also helped in homogenising the glass melt. For homogenising temperature around 1300°C the glass can not be kept for long because of two reasons. Firstly the fluid glass at these temperatures has a tendency to react with the crucible and secondly there may be a loss of PbO, in the form of vapours, affecting the refractive index of the glass composition.

The glass was fluid enough at 1200°C but was heated to 1300°C to obtain a larger cooling range to affect rapid cooling of the glass melt when poured in the water cooled aluminum mold and prevent devitrification. Glass could have been produced by quenching into water but this was avoided to ensure less chances of bubbles in the glass particles before they are spheroidised.

### 5.3 Classification of the Glass Powder:

Sedimentation techniques have been observed to be superior to wet sieving. Powder collected over 400 #, ASTM sieve number, had fairly large number of particles below 40 microns. In Table glass powder Sample-B obtained by using sedimentation technique can be seen to have only 16.4 percent particles below 35 microns.

#### 5.4 Spheroidisation:

Glass Microsphere making furnace has been quite satisfactory for particles above 40 microns, since there were no particles observed escaping with the hot gases from the bottom of the collection chamber.

In the powder sample containing particles below 40 microns, fines were observed to be carried away with the hot gases. Though it was not an appreciable amount and therefore the problem was not too serious but an idea of using water sealing at the bottom end of the collection chamber will produce better results.

Cooling of the collection chamber itself by constantly spraying water on the outside walls is important. Arrangements for cooling the chamber by circulating coils or doubles walls for water circulation will improve matters. Cold collection chamber is required for the air quenching of the molten glass spheres when they come out of the hot zone.

Feed rates of 0.98 g/mt. and 1.9 g/mt. for Sample -A and Sample -B respectively, as was seen in Table -1, were found to be satisfactory for spheroidisation.

Although the conditions recorded for the maximum spheroidisation for Sample-B show a higher temperature profile than for Sample -A as shown in Fig. 5, reduced bubble formation in the spheroidised Sample -D as compared to Sample -C is most probably due to its coarser size. The bubble formation tendency in the sample could be reduced by increasing the air flow rate which will reduce the residence of the powder in the flame.

### 5.5 Physical Characteristics:

Glass in the system  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$  and  $\text{ZnO}$  when prepared in platinum or sintered alumina crucible had a light yellow colour. Whereas, when it was prepared in massive amount in nonporous, fireclay crucible it picked up an amber colour. This coloration is thought to be due to some coloring element picked up by the glass melt from the crucible, as an impurity. This could be due to small amount of Fe present in the fireclay or feldspar used in the making the crucibles.

Decrease in the density of spheroidised glass powder can be associated with the bubble formation in the glass spheres. Lower density of Sample -C is due to a greater degree of bubble formation.

Refractive index of the spheroidised as well as unspheroidised glass powder, determined by Becke Line method is greater than 2.1. The highest refractive index of the standard liquids available was 2.1.

### 5.6 Reflectivity Measurements:

Reflectivity apparatus has given satisfactory results except for two instances in Figs. 10 and 13 where the displacement of the peaks in angular distribution of percent reflectivity from the expected positions can be attributed to the nonalignment of the collimated incident beam of light with axis of the specimen holder. Slight shift of the angle of the incident light could have displaced the position of the peaks that should be at  $\theta_1 = 0^\circ$  in Fig. 10 and at  $\theta_1 = 0^\circ, 10^\circ$  and  $20^\circ$  in Fig. 13.

In all the curves for angular distribution of percent reflectivity for the coated surfaces two distinct peaks due to reflex and specular reflection can be seen. These peaks have been separated to examine them clearly. In the peak for  $\theta_2 = 0^\circ$  there is a combined effect of reflex and specular reflection and the height of the peak is greater than for  $\theta_2 = 5^\circ$  and  $\theta_2 = 10^\circ$  for which the peaks are well separated.

For most of the coated surfaces e.g. in Fig. 8, corresponding to the specular reflection only, observed for  $\theta_2 = 10^\circ$ , is smaller than the peak observed for  $\theta_2 = 5^\circ$  and  $\theta_2 = 0^\circ$ . This may be expected since intensity of the reflected light due to reflex-reflection does add up here.

As for as the effect of the size of glass spheres is concerned 22 micron glass spheres have shown better results than 52 micron spheres, Figs. 8 and 9. No suitable explanation for this difference is available.

Blank surfaces show specular reflection only and the peaks observed at different values of  $\theta_2$  are several times higher than specular peaks observed for the coated surfaces, as can be seen in Figs. 8 and 15.

Since reflex-reflectivity of a coated surface depends upon the area occupied by the glass spheres and percent fraction of the bright spheres, the term absolute reflectivity which has been defined earlier has been taken as a common bases for comparing different surfaces.

For the said purpose absolute reflectivity i.e. a term taking into consideration the percent reflectivity, percent area occupied by the spheres and percent bright spheres at the conditions of minimum illumination has been used for comparing the coated surfaces with glass microspheres with the commercial reflex-reflecting sheet taken as a standard. The results for  $\theta_2 = 10^\circ$ , where specular and reflex-reflection peaks are well separated, as seen in Fig. 17, show that the characteristic of the buffed aluminum surface coated with 52 micron glass spheres is compareable with the commercial sheet. But the mirror and non-reflecting black paper coated with 52 micron spheres are about one fifth as efficient as the standard commercial sheet.

The plot of Fig. 17 is useful only for the peaks due to reflex-reflection since corrections in absolute reflectivity have been meant for the same. Therefore similar curves were not plotted for the surfaces coated with 22 micron glass spheres but efficiencies of all these coated surfaces have been compared with the commercial reflex-reflecting sheet taken as 100 percent efficient in Table -10.

In Table -10 only the peak values of percent reflectivities from Figs. 8 to 14, for  $\theta_2 = 10^\circ$  have been used for comparing various efficiencies. Four important observations may be made from this table as noted below,

- (a) The buffed aluminum surface coated with 22 micron glass spheres showed higher efficiency than the commercial sample.



- (b) The buffed aluminum surface coated with 52 microns glass spheres showed an efficiency compareable with the commercial sheet.
- (c) The mirror surface shows lesser efficiency than above two cases.
- (d) The non-reflecting black paper surface coated with 22 micron glass spheres has shown about 50 percent efficiency.

The observation 'a' is probably due to the absence of transparent covering layer as compared to the commercial sample. This may be resulting in a reduced intensity in the commercial sample.

The observation 'b' can probably be due to some size effect but no conclusive explanation is available. The observation 'c' is due to the large distance between the layer of sphere surface and reflecting mirrored surface which is approximately of the order of  $1/8$ th of an inch.

The observation 'd' which is interesting indicates that these spherical powders when layed on non-reflecting backing surface are capable of providing sufficient reflex-reflection action.



## 6. CONCLUSIONS

- (a) Glass prepared in the system  $\text{PbO-TiO}_2\text{-BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-ZnO}$  has refractive index greater than 2.1.
- (b) Glass powder in the size range 10-80 microns was spheroidised under suitable conditions using an oxy-acetylene burner.
- (c) Surfaces coated with spheroidised powder showed reflex-reflective characteristics compareable with a commercial reflex-reflective material.
- (d) Spherical particles in the lower size range showed almost twice the reflectivity than those of the higher size range.
- (e) These spherical powders are capable of showing sufficient reflex-reflection action even when coated on non-reflecting or rough surfaces.

## BIBLIOGRAPHY

1. G.A. Van Lear Jr., 'Reflectors used in Highway Signs and Warning Signals', Part I, II and III', Jn. of Optical Society of America, 30 (10) 462, 1940.
2. P.V. Palniquist, B.S. Cross and G.P. Netherly, 'Reflex Light Reflectors', U.S. 2, 407, 680, Sept. 17, 1946.
3. D.M. Finch, 'Reflex Reflector Performance Critical', Highway Research Board Bulletin 34, 1951.
4. James H. Havens and Aalice C. Peed, 'Spherical Lens Optics applied to Retrodirective Reflection', Highway Research Board Bulletin 56, Jan. 1952.
5. P.V. Palniquist and Raymond E. Penrod, 'Reflex Light Reflector', U.S. 2, 543, 800, March 6, 1951.
6. Nelson W. Taylor, 'Reflex Light Reflectors and Glass Bead Elements Thereof', U.S. 2, 713, 286, July 19, 1955.
7. P.V. Palniquist and W.R. Beck, 'Glass Beads Hemispherically Reflectorised with Metallic Coating and Compositions Thereof', U.S. 2, 963, 378, Dec. 6, 1960.
8. Eduard R. de Vries, Flemington, N.J. and Alistair J. Ross, 'Retro-Reflective Particles and Reflective Markers and Compositions containing such Particles', U.S. 3, 254, 563, June 7, 1966.
9. Eduard R. De Vries, 'Colored Reflective Coating Composition', U.S. 3, 288, 618, Nov. 29, 1966.
10. Samuel E. Wissinger, Jr., 'Reflectorising Glass Spheres and Methods of Making them', U.S. 3, 291, 633, Dec. 13, 1966.
11. H. Rawson, 'Inorganic Glass Forming Systems', London, New York Academic Press, 1967.
12. Maurice L. Huggin, 'The Refractive Index of Silicate Glasses as a Function of Composition', Jn. of Optical Soc. of America, 30, 495, (10) 1940.
13. Warren R. Beck, Mahtomedi and Nelson W. Taylor, 'High Index Glass Elements', U.S. 2, 726, 161, Dec. 6, 1955.
14. Warren R. Beck, Mahtomedi and Nelson W. Taylor, 'High Index Glass Elements', U.S. 2, 842, 446, July 8, 1958.

15. Warren R. Beck, Mahtomedi and Nelson W. Taylor, 'High Index Glass Elements', U.S. 2, 853, 393, Sept. 23, 1958.
16. Guy E. Rindone, 'Glass Composition', U.S. 2, 939, 797, June 7, 1960.
17. Vincent L. Duval Adrian, 'Large Dia High n Glass Beads', U.S. 3, 041, 191, June 26, 1962.
18. E.M. Alexander, C.S. Searight and J.R. Ryan, 'High Titanate Glasses', Belg. 652, 095, Dec. 16, 1964.
19. Vincent L. Duval d' Adrian, 'High Alkali Earth Oxide Glass Bead Composition', U.S. 3, 306, 757, Feb. 28, 1967.
20. A.M. Gasparyan and A.A. Zaminyan, 'A Method of Formation of Spherical Glass Particles of Small Dimensions', Doklady Akad. Nauk Arman. S.S.R., 23, 67-9 (1956) (Abs.)
21. Alfred D. Pinotti, 'Method for Producing Glass Beads', U.S. 2, 963, 824, Dec. 13, 1960.
22. H.L. Robinson, 'Glass Making Furnace', U.S. 3, 133, 805, May 19, 1964.
23. C.E. Searight, Hugh W. Smalley and Hyman L. Robinson, 'Method and Apparatus for Manufacturing Glass Beads', U.S. 3, 138, 444, June 23, 1964.
24. E.L. Schmidt, 'Glass Bead Furnace and Method of Making Glass Beads', U.S. 3, 190, 737, June 22, 1965.
25. K.K. Verma, 'A Study in the Preparation and Characterisation of Spherical Glass Particles in the Subsieve Range', B.Tech. Thesis, P. 42, 46, Dept. of Metallurgical Engg., Indian Institute of Technology, Kanpur, May 1968.
26. R.C. Emmons and R.M. Gates, 'The use of Backline Colors in Refractive Index Determinations, American Minerologist, 33, 612-18, 1948.
27. Kuan-Han Sun, 'Lead - Titanate - Borate Glass', U.S. 2, 472, 447, June 7, 1949.
28. B.S. Cross, 'Bead Coated Tympon Sheet', U.S. 2, 555, 319, June 5, 1951.
29. J.E. Stanworth and A.E. Dale, 'Glass Composition', U.S. 2, 615, 817, Oct. 28, 1952.
30. Frank L. Porth, 'Method of Producing Reflecting Films, Decalomanias and Signs', U.S. 2, 646, 364, July 21, 1953.

31. C.E. Searight, 'Production of Silicon Coated Glass Beads', U.S. 2, 730, 841, Jan. 17, 1956.
32. H.H.Holscher, 'Glass-its Transparency and Structure, Glass Industry 3, 81-9, 110-14, 1958.
33. Glaverbel, 'Glass with High Refractive Index', Neth. Appl. 6, 602, 030, Aug. 25, 1966.

## APPENDIX A

RESULTS SHOWN IN TABULATED AND GRAPHICAL FORM

TABLE - 1

CONDITIONS FOR MAXIMUM SPHEROIDISATION OF GLASS POWDER  
SAMPLES

Glass powder sample	Flow rate of gases			Powder feed g/mt.
	Oxygen (lit./mt.)	Acetylene (lit./mt.)	Air (lit./mt.)	
Sample - A,				
Glass particles below 40-microns	4.35	5.07	24.5	0.98
Sample - B,				
Glass particles above 40 microns	4.35	5.22	24.5	1.9

TABLE - 2

SIZE DISTRIBUTION OF UNSPHEROIDISED GLASS PARTICLES  
BELOW 40 MICRONS IN SAMPLE - A.

Size range, (in microns)	Frequency in percent by number	Size-X, (in microns)	Percent by number finer than X.
Below 10	6.5	10	6.5
10 - 12.5	10	12.5	16.5
12.5- 15	8	15	24.5
15 - 17.5	8.5	17.5	33
17.5- 20	8	20	41
20 - 22.5	9.5	22.5	50.5
22.5- 25.5	7.5	25	58
25 - 27.5	10.5	27.5	58.5
27.5- 30	6.5	30	75
30 - 32.5	7.5	32.5	82.5
32.5- 35	2.5	35	85
35 - 37.5	4	37.5	89
37.5- 40	1.5	40	90.5



TABLE - 3

SIZE DISTRIBUTION OF UNSPHEROIDISED GLASS PARTICLES  
ABOVE 40 MICRONS IN SAMPLE - B

Size range, (in microns)	Frequency in percent by number	Size - X (in microns)	Percent by number finer than X.
Below 35	16.4	35	16.4
35 - 40	9.2	40	25.6
40 - 45	9.2	45	34.8
45 - 50	10.2	50	45.2
50 - 55	6.8	55	52.0
55 - 60	9.6	60	61.6
60 - 65	12.4	65	74.0
65 - 70	6	70	80.0
70 - 75	5.6	75	85.6
75 - 80	3.6	80	89.2

TABLE - 4

## SIZE DISTRIBUTION OF GLASS SPHERES IN SAMPLE - C

Size range (in microns)	Frequency in percent by number	Size-X (in microns)	Percent by number finer than X.
Below 10	2	10	2
10 - 12.5	5.5	12.5	7.5
12.5 - 15	6.5	15	14
15 - 17.5	10	17.5	24
17.5 - 20	18.5	20	42.5
20 - 22.5	23	22.5	65.5
22.5 - 25	19	25	84.5
25 - 27.5	7	27.5	91.5
27.5 - 30	6	30	97.5

TABLE - 5

## SIZE DISTRIBUTION OF GLASS SPHERES IN SAMPLE - D

Size ranges (in micron)	Frequency in percent by number	Size - X, (in microns)	Percently number finer than X
42.5-45	6.5	45	6.5
45 -47.5	12	47.5	18.5
47.5-50	23	50	41.5
50 -52.5	19.5	52.5	61
52.5-55	23	55	84
55 -57.5	8	57.5	92
57.5-60	2.5	60	94.5
60 -62.3	3	62.5	97.5
62.5-65	1.5	65	99

TABLE - 6 (a)

REFLEX - REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR DISTRIBUTION OF PERCENT REFLECTIVITY FOR 22 MICRON GLASS SPHERES COATED ON A BUFFED ALUMINIUM SURFACE

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (for $I_0 = 890$ )
20	0	1.063	3.45	0.447
15	0	1.035	4.5	0.523
10.5	0	1.017	5.0	0.572
7.5	0	1.009	12.1	1.371
4.5	0	1.004	52.8	5.97
2.5	0	1.000	128.	14.37
0.5	0	1.000	294.	33.08
-20.	0	1.063	3.5	0.418
-15	0	1.035	5.75	0.668
-10.5	0	1.017	11.5	1.315
20	5	1.100	2.75	0.34
15	5	1.061	1.25	0.149
10.5	5	1.034	3.5	0.407
7.5	5	1.022	6.92	0.795
4.5	5	1.011	14.3	1.624
2.5	5	1.007	32.9	3.73
0.5	5	1.002	46.7	5.26
-20	5	1.032	10.0	1.16
-15	5	1.023	88.	1.002
-12	5	1.004	185.	20.88
-10.5	5	1.002	232.5	26.16
20	10	1.137	2.5	0.319
15	10	1.086	3.75	0.458
10.5	10	1.051	2.75	0.325
7.5	10	1.033	6.5	0.754
4.5	10	1.017	9.5	1.087
2.5	10	1.009	22.5	2.55
0.5	10	1.002	41.5	4.67
-25	10	1.020	104.	11.93
-20	10	1.00	207.5	23.33
-17	10	0.992	127.5	14.42
-15	10	0.988	37.	4.11
-10.5	10	0.9848	10.	1.106

- $\theta_1$  is the angle made by normal to the photocell with incident beam of light.  
 $\theta_2$  is the angle made by normal to the coated surface with incident beam of light.  
 I, is the intensity of the light beam reflected from the coated

TABLE - 6(b)

REFLEX - REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR  
DISTRIBUTION OF PERCENT REFLECTIVITY FOR 52 MICRON GLASS  
SPHERES COATED ON A BUFFED ALUMINUM SURFACE

$\theta_1$ in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (for $I_0 = 890$ )
20	0	1.063	2.75	0.328
15	0	1.035	4.	0.466
10.5	0	1.017	6.	0.686
7.5	0	1.009	9.32	1.079
4.5	0	1.004	22.92	2.59
2.5	0	1.00	122.8	12.26
0.5	0	1.00	173.	19.44
-20	0	1.063	3.5	0.418
-15	0	1.035	4.	0.466
-10.5	0	1.017	8.25	0.943
20	5	1.10	2.75	0.319
15	5	1.061	3.5	0.417
10.5	5	1.034	4.25	0.494
7.5	5	1.022	7.35	0.845
4.5	5	1.011	15.14	1.72
2.5	5	1.007	29.84	3.38
0.5	5	1.002	35.48	3.995
-20	5	1.032	4.75	0.551
-15	5	1.023	34.5	3.96
-12	5	1.004	112.5	12.72
-10.5	5	1.002	137.5	15.49
20	10	1.137	2.5	0.319
15	10	1.086	3.	0.366
10.5	10	1.051	3.5	0.413
7.5	10	1.033	6.42	0.802
4.5	10	1.017	9.08	1.037
2.5	10	1.009	18.17	2.06
0.5	10	1.002	32.	3.62
-25	10	1.020	12.5	1.433
-20	10	1.00	135.	15.17
-17	10	0.992	95.	10.67
-15	10	0.988	29.	3.22
-10.5	10	0.9848	7.25	0.802

TABLE - 6(c)

REFLEX-REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR  
DISTRIBUTION OF PERCENT REFLECTIVITY FOR 22 MICRON  
GLASS SPHERES COATED ON A NON-REFLECTING BLACK PAPER

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0=870$ )
20	0	1.063	4.25	0.519
15	0	1.035	4.75	0.565
10.5	0	1.017	4.5	0.526
7.5	0	1.009	12.12	1.405
4.5	0	1.004	13.84	1.60
2.5	0	1.00	17.3	1.99
0.5	0	1.00	16.44	1.89
- 20	0	1.063	4.25	0.519
- 15	0	1.035	4.75	0.565
-10.5	0	1.017	5.5	0.643
20	5	1.10	3.75	0.474
15	5	1.061	4.5	0.549
10.5	5	1.034	4.75	0.565
7.5	5	1.022	12.97	1.524
4.5	5	1.011	14.7	1.709
2.5	5	1.007	15.57	1.805
0.5	5	1.002	15.57	1.795
- 20	5	1.032	4.5	0.534
- 15	5	1.023	5.	0.588
- 12	5	1.004	5.25	0.606
- 10.5	5	1.002	5.75	0.662
20	10	1.137	3.5	0.458
15	10	1.086	3.75	0.468
10.5	10	1.051	4.5	0.543
7.5	10	1.033	11.24	1.335
4.5	10	1.017	12.97	1.519
2.5	10	1.009	15.57	1.807
0.5	10	1.002	15.57	1.794
- 30	10	1.02	4.75	0.556
- 25	10	1.00	4.75	0.546
- 20	10	0.992	4.75	0.541
- 15	10	0.988	6.5	0.738
- 10.5	10	0.9848	6.5	0.736



TABLE - 6(d)

REFLEX-REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR  
DISTRIBUTION OF PERCENT REFLECTIVITY FOR 52 MICRON  
GLASS SPHERES COATED ON A NON-REFLECTING BLACK PAPER

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0 = 890$ )
20	0	1.063	2.5	0.299
15	0	1.035	2.5	0.291
10.5	0	1.017	1.5	0.172
7.5	0	1.009	4.76	0.54
4.5	0	1.004	4.32	0.588
2.5	0	1.00	4.76	0.535
0.5	0	1.00	3.46	0.389
- 20	0	1.063	1.75	0.209
- 15	0	1.035	2.0	0.233
- 10.5	0	1.017	2.5	0.286
20	5	1.10	2	0.247
15	5	1.061	2.5	0.298
10.5	5	1.034	1.5	0.174
7.5	5	1.022	3.46	0.397
4.5	5	1.011	3.46	0.393
2.5	5	1.007	3.46	0.392
0.5	5	1.002	2.6	0.293
- 20	5	1.032	2.5	0.29
- 15	5	1.023	2.75	0.316
- 12	5	1.004	2.75	0.314
- 10.5	5	1.002	4.	0.451
20	10	1.137	1.75	0.224
15	10	1.086	1.5	0.183
10.5	10	1.051	2.0	0.236
7.5	10	1.033	4.76	0.552
4.5	10	1.017	3.46	0.396
2.5	10	1.009	3.46	0.393
0.5	10	1.002	4.76	0.536
- 25	10	1.02	2.5	0.287
- 20	10	1.00	2.5	0.281
- 17	10	0.992	2.75	0.306
- 15	10	0.988	2.75	0.305
- 10.5	10	0.9848	2.75	0.304

TABLE - 6(e)

REFLEX-REFLECTIVE CHARACTERISTICS INTERMS OF ANGULAR DISTRIBUTION OF PERCENT REFLECTIVITY FOR 22 MICRON GLASS SPHERES COATED ON A MIRROR SURFACE

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0 = 870$ )
20	0	1.063	5.25	0.642
15	0	1.035	7.	0.833
10.5	0	1.017	8.	0.936
7.5	0	1.009	122.8	14.24
4.5	0	1.004	154	17.8
2.5	0	1.000	190.3	20.87
0.5	0	1.000	159.2	18.32
- 20	0	1.063	6.75	0.825
- 15	0	1.035	9.25	1.100
- 10.5	0	1.017	23	2.69
20	5	1.100	4.25	0.537
15	5	1.061	4.5	0.549
10.5	5	1.034	4.5	0.535
7.5	5	1.022	9.52	1.17
4.5	5	1.011	11.24	1.308
2.5	5	1.007	12.1	1.403
0.5	5	1.002	11.24	1.295
- 20	5	1.032	15.25	1.81
- 15	5	1.023	162.5	19.1
- 12	5	1.004	165.	19.06
- 10.5	5	1.002	155	17.86
20	10	1.137	3.5	0.458
15	10	1.086	4.0	0.499
10.5	10	1.051	3.5	0.423
7.5	10	1.033	0.48	0.77
4.5	10	1.017	6.92	0.81
2.5	10	1.009	6.92	0.803
0.5	10	1.002	7.78	0.895
- 30	10	1.051	14.5	1.751
- 25	10	1.018	170.	19.9
- 20	10	1.000	150	17.25
- 15	10	0.988	20	2.27
- 10.5	10	0.9848	12.75	1.44

TABLE - 6(f)

REFLEX-REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR DISTRIBUTION OF PERCENT REFLECTIVITY FOR 52 MICRON GLASS SPHERES ON A MIRROR SURFACE.

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity For ( $I_0 = 890$ )
20	0	1.063	4.00	0.478
15	0	1.031	4.75	0.553
10.5	0	1.017	6.25	0.636
7.5	0	1.009	7.78	0.883
4.5	0	1.004	12.1	1.216
2.5	0	1.000	16.42	1.846
0.5	0	1.000	26.8	3.01
- 20	0	1.063	4.5	0.537
- 15	0	1.035	6.0	0.698
- 10.5	0	1.017	8.25	0.944
20	5	1.100	3.75	0.464
15	5	1.061	4.75	0.567
10.5	5	1.034	4.00	0.465
7.5	5	1.022	7.35	0.852
4.5	5	1.011	7.78	0.885
2.5	5	1.007	10.38	1.175
0.5	5	1.002	8.2	0.924
- 20	5	1.032	6.5	0.755
- 15	5	1.023	50.0	5.75
- 12	5	1.004	225	25.4
- 10.5	5	1.002	250	28.14
20	10	1.137	3.00	0.383
15	10	1.086	3.25	0.396
10.5	10	1.051	3.25	0.384
7.5	10	1.033	6.05	0.703
4.5	10	1.017	6.92	0.792
2.5	10	1.009	6.92	0.785
0.5	10	1.002	6.48	0.73
- 25	10	1.020	51.	5.85
- 20	10	1.000	225.	25.3
- 17	10	0.992	155.	17.28
- 15	10	0.998	28.5	3.16
- 10.5	10	0.9848	10.25	1.135

TABLE - 6(g)

REFLEX-REFLECTIVE CHARACTERISTICS IN TERMS OF ANGULAR DISTRIBUTION OF PERCENT REFLECTIVITY OF A COMMERCIAL REFLEX-REFLECTING SHEET.

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0=870$ )
20	0	1.063	6.25	0.764
15	0	1.035	7.	0.834
10.5	0	1.017	8.	0.936
7.5	0	1.009	10.81	1.256
4.5	0	1.004	18.17	2.094
2.5	0	1.00	36.3	4.17
0.5	0	1.00	67.5	7.76
- 20	0	1.063	5.25	0.642
- 15	0	1.035	6.5	0.774
- 10.5	0	1.017	9.75	1.14
20	5	1.1	5.5	0.632
15	5	1.061	6.5	0.793
10.5	5	1.034	7.75	0.921
7.5	5	1.022	10.38	1.22
4.5	5	1.011	15.14	1.76
2.5	5	1.007	24.22	2.81
0.5	5	1.002	53.7	6.19
- 20	5	1.032	6.5	0.771
- 15	5	1.023	15.5	1.823
- 12	5	1.004	25.	2.89
- 10.5	5	1.002	27.	3.11
20	10	1.137	5.	0.655
15	10	1.086	6.	0.749
10.5	10	1.051	7.	0.845
7.5	10	1.033	9.95	1.18
4.5	10	1.017	13.4	1.569
2.5	10	1.009	24.67	2.858
0.5	10	1.002	53.7	6.18
- 30	10	1.051	6.	0.725
- 25	10	1.018	15.	1.755
- 20	10	1.000	24.5	2.82
- 15	10	0.988	9.25	1.051
- 10.5	10	0.9848	9.5	1.074

TABLE - 6(h)

REFLECTING CHARACTERISTICS IN TERMS OF ANGULAR DISTRIBUTION  
OF PERCENT REFLECTIVITY OF BLANK BUFFED ALUMINUM SURFACE  
USED AS A REFLECTIVE BACKING FOR GLASS SPHERES

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0 = 930$ )
7.5	5	1.022	3.29	0.428
4.5	5	1.011	4.76	0.518
2.5	5	1.007	5.19	0.563
0.5	5	1.002	4.32	0.466
- 20	5	1.032	6.5	0.722
-15	5	1.023	200.	22.0
-10.5	5	1.002	530	57.2
7.5	10	1.033	3.03	0.336
4.5	10	1.017	3.03	0.332
0.5	10	1.002	2.59	0.299
- 25	10	1.02	81.	8.74
- 20	10	1.00	620.	66.7
- 15	10	0.988	165.	17.53
- 10.5	10	0.9848	19.5	2.065

TABLE - 6(1)

REFLECTING CHARACTERISTICS IN TERMS OF ANGULAR DISTRIBUTION OF PERCENT REFLECTIVITY OF THE MIRROR SURFACE USED AS A REFLECTIVE BACKING SURFACE FOR GLASS SPHERES

$\theta_1$ (in degrees)	$\theta_2$ (in degrees)	$\frac{\cos \theta_2}{\cos  \theta_1 + \theta_2 }$	I	Percent reflectivity (For $I_0=930$ )
20	0	1.063	2.5	0.269
15	0	1.035	3.	0.334
10.5	0	1.017	2.5	0.274
7.5	0	1.009	4.76	0.517
4.5	0	1.004	177.4	19.19
2.5	0	1.00	519.	55.8
0.5	0	1.00	675.	72.6
- 20	0	1.063	2.75	0.314
- 15	0	1.035	2.5	0.278
- 10.5	0	1.017	4.5	0.492
20	5	1.1	1.75	0.207
15	5	1.061	2.5	0.285
10.5	5	1.034	1.75	0.1958
- 20	5	1.032	3.5	0.388
- 15	5	1.023	94	10.34
- 12	5	1.004	660	71.4
- 10.5	5	1.002	840	90.5
20	10	1.137	2.75	0.336
15	10	1.086	2.	0.233
10.5	10	1.051	1.5	0.17
- 25	10	1.02	97.	10.64
- 20	10	1.00	890.	95.7
- 17	10	0.992	740.	78.9
- 15	10	0.986	235	25.
- 10.5	10	0.9848	5.	0.53



TABLE - 7

PERCENT AREA OCCUPIED BY THE GLASS SPHERES ON THE COATED SURFACES USED FOR THE STUDY OF THEIR REFLEX-REFLECTIVE CHARACTERISTICS

Sample	Number of particles on 1 cm <sup>2</sup> area of the Eye Piece*, x	Percent area occupied by the Glass Spheres ( $4\pi 10^{-4} d^2 x$ )**
Buffed aluminum Surface coated with 22 micron glass spheres	35	21
Buffed aluminum surface coated with 52 micron glass spheres	9.5	32
Non-reflecting Black paper coated with 22 micron glass spheres	40.6	25
Non-reflecting black paper coated with 52 micron glass spheres	4.75	16
Mirror coated with 22 micron glass spheres	22	13
Mirror coated with 52 micron glass spheres	6.9	23
Commercial reflex-reflecting sheet with 65 micron glass spheres	6.76	35.9

\* Magnification of Eye piece 10X and objective 40X.

\*\* d is the average size of the glass spheres in microns

TABLE - 8

PERCENT BRIGHT GLASS SPHERES IN 22 MICRON, 52 MICRON  
 SAMPLES AND IN THE SPHERES COATED ON THE COMMERCIAL  
 REFLEX-REFLECTING SHEET AT DIFFERENT CONDITIONS OF  
 ILLUMINATION.

Sample	Percent Bright spheres at Magnification			
	50	100	200	400
22 Micron glass spheres	73.33	79.9	87.5	96.86
52 Micron glass spheres	72.7	85.5	90.06	100
65 Micron glass spheres used on the commercial reflex reflecting sheet.	91.94	91.55	91.8	94

TABLE - 9

REFLEX-REFLECTIVE CHARACTERISTICS\* IN TERMS OF ANGULAR DISTRIBUTION OF ABSOLUTE  
REFLECTIVITY FOR SURFACES COATED WITH 52 MICRON CLASS SPHERES

$\theta_1$ (in degrees)	Commercial Reflex- reflecting sheet		A buffed alumi- num surface coated with 52 micron glass spheres		A mirror surface coated with 52 micron glass spheres		A non-reflecting black paper coated with 52 micron glass spheres	
	Percent reflec- tivity	Absolute reflec- tivity	Percent reflec- tivity	Absolute reflec- tivity	Percent reflec- tivity	Absolute reflec- tivity	Percent reflec- tivity	Absolute reflec- tivity
20	0.655	1.984	0.319	1.37	0.383	2.29	0.224	1.926
15	0.749	2.27	0.366	1.57	0.396	2.37	0.183	1.574
10.5	0.845	2.56	0.413	1.77	0.384	2.3	0.236	2.03
7.5	1.18	3.58	0.802	3.45	0.703	4.24	0.552	4.75
4.5	1.569	4.75	1.037	4.46	0.792	4.74	0.396	3.41
2.5	2.858	8.66	2.06	8.86	0.785	4.7	0.393	3.38
0.5	6.48	18.74	3.62	15.56	0.73	4.37	0.536	4.61
30	0.725	2.19	---	---	---	---	---	---
25	1.755	5.32	1.433	6.16	5.85	35	0.287	2.47
20	2.82	8.55	1.517	6.53	25.3	151.4	0.281	2.42
17	---	---	10.67	45.9	17.28	103.2	0.306	2.63
15	1.051	3.19	3.22	13.84	3.163	18.92	0.305	2.62
10.5	1.074	3.25	0.802	3.45	1.135	6.8	0.304	2.61

\*  $\theta_1$  is the angle made by the normal to the photocell with the incident beam of light.

TABLE - 10

**EFFICIENCY OF THE REFLEX-REFLECTING SURFACES COATED WITH 22 AND 52 MICRON GLASS SPHERES AS COMPARED WITH THE COMMERCIAL REFLEX-REFLECTING SHEET**

Sample	Percent area occupied by glass spheres	Percent bright spheres	Percent reflectivity*	Absolute reflectivity	Percent efficiency
1. The commercial reflex reflecting sheet	35.9	91.4	6.18	18.7	100
2. A buffed aluminum surface coated with 22 micron glass spheres	21	73.33	4.67	30.3	162
3. Mirror surface coated with 22 micron glass spheres	13	73.33	0.895	9.4	50.3
4. Non-reflecting black paper coated with 22 micron glass spheres	25	73.33	1.83	9.98	53.3
5. A buffed aluminum surface coated with 52 glass spheres	32	72.7	3.62	15.56	83.1
6. Mirror surface coated with 52 micron particles	23	72.7	0.792	4.74	25.4
7. Non-reflecting black paper coated with 52 micron glass spheres	16	72.7	0.552	4.47	23.9

\* Percent spheres counted at magnification 50X.

TABLE - 11

## REPRESENTATIVE PHOTOMICROGRAPHS OF THE GLASS POWDER SAMPLES

Picture No.	Glass Powder Sample (Details of the picture)	Magnification	Distance representing 50 microns
1.	A Unspheroidised particles below 40 microns	100 X	0.5 Cm.
2.	C 22 mirror spheres in spheroidised Sample A	100 X	0.5 Cm.
3.	C Bubbles in 22 micron spheres	300 X	1.5 Cm.
4.	B Unspheroidised particles above 40 microns	100 X	0.5 Cm.
5.	D 52 Micron spheres in spheroidised sample-B	100 X	0.5 Cm.
6.	D Bubbles in 52 micron glass spheres	200 X	1.0 Cm.

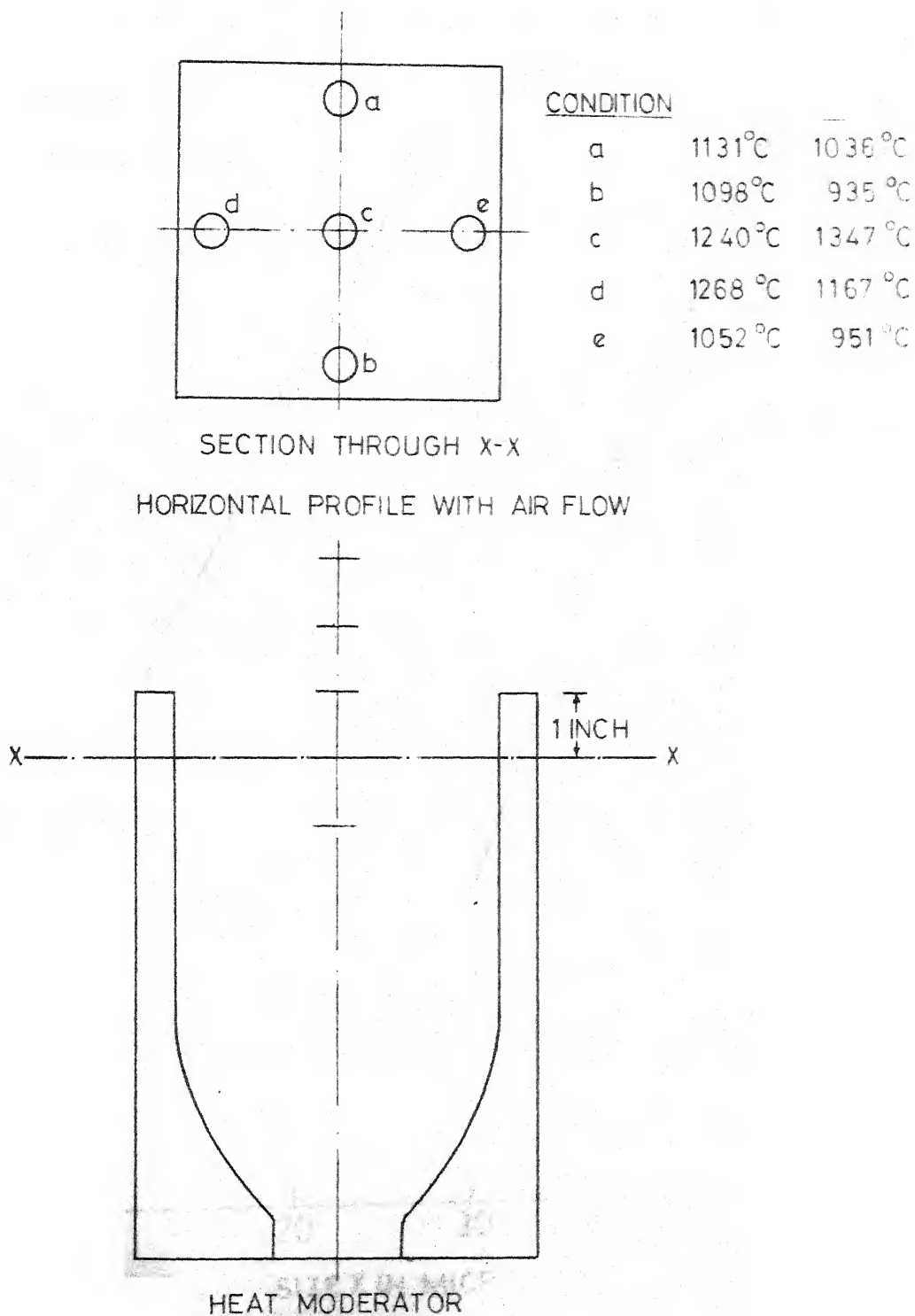
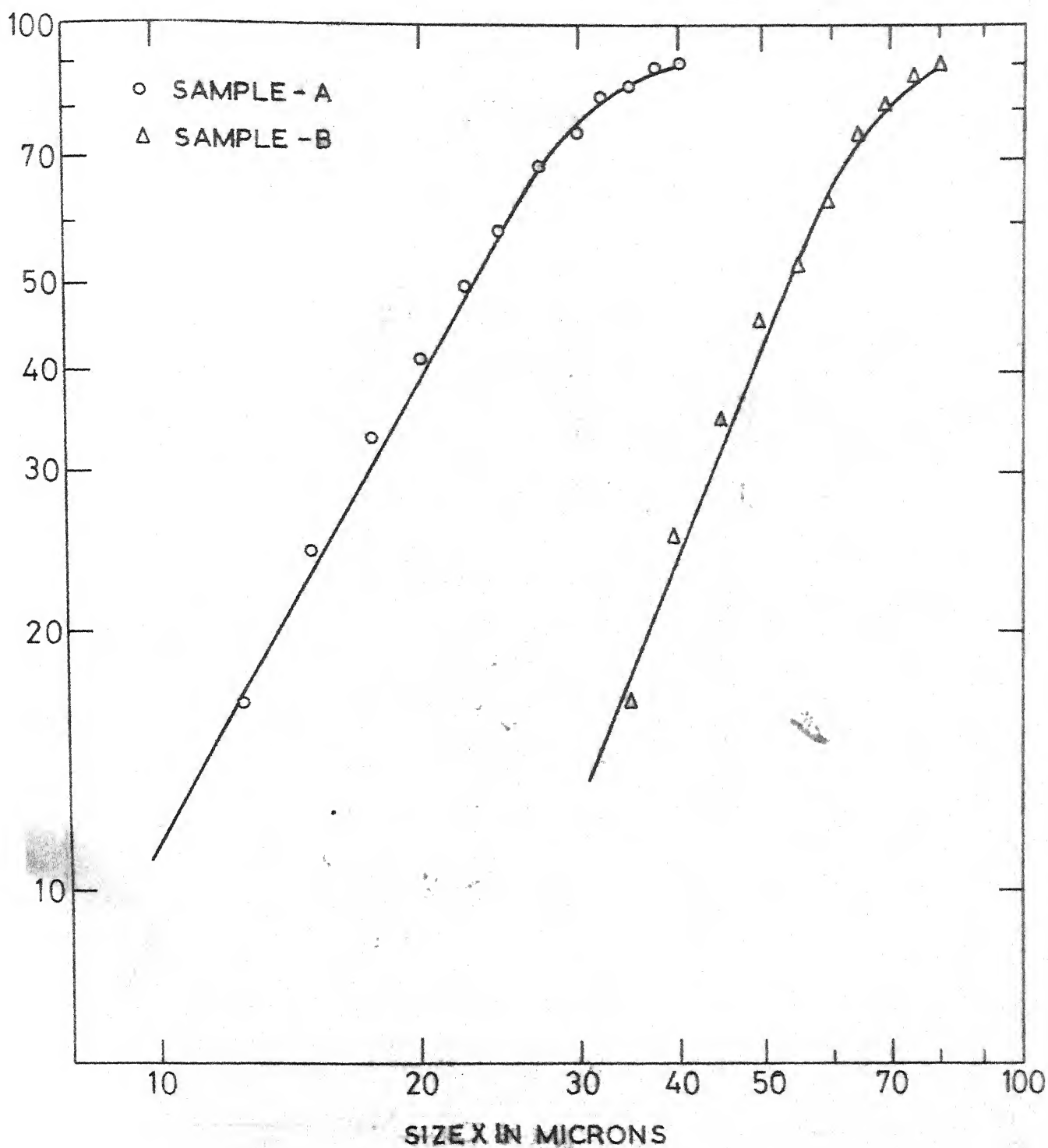
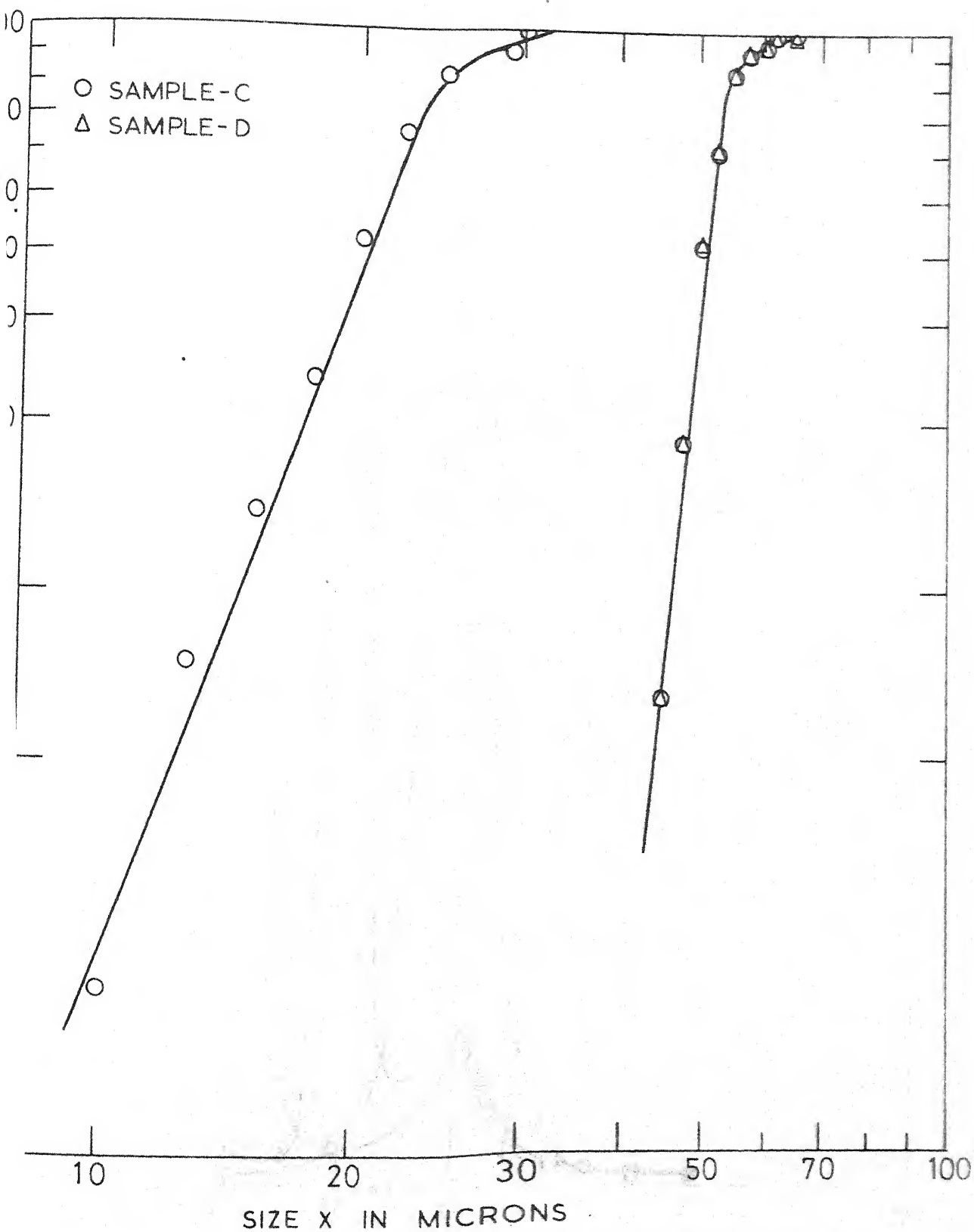


FIG. 5 TEMPERATURE PROFILE OF THE HOT ZONE FOR DIFFERENT CONDITIONS OF SPHEROIDISATION.

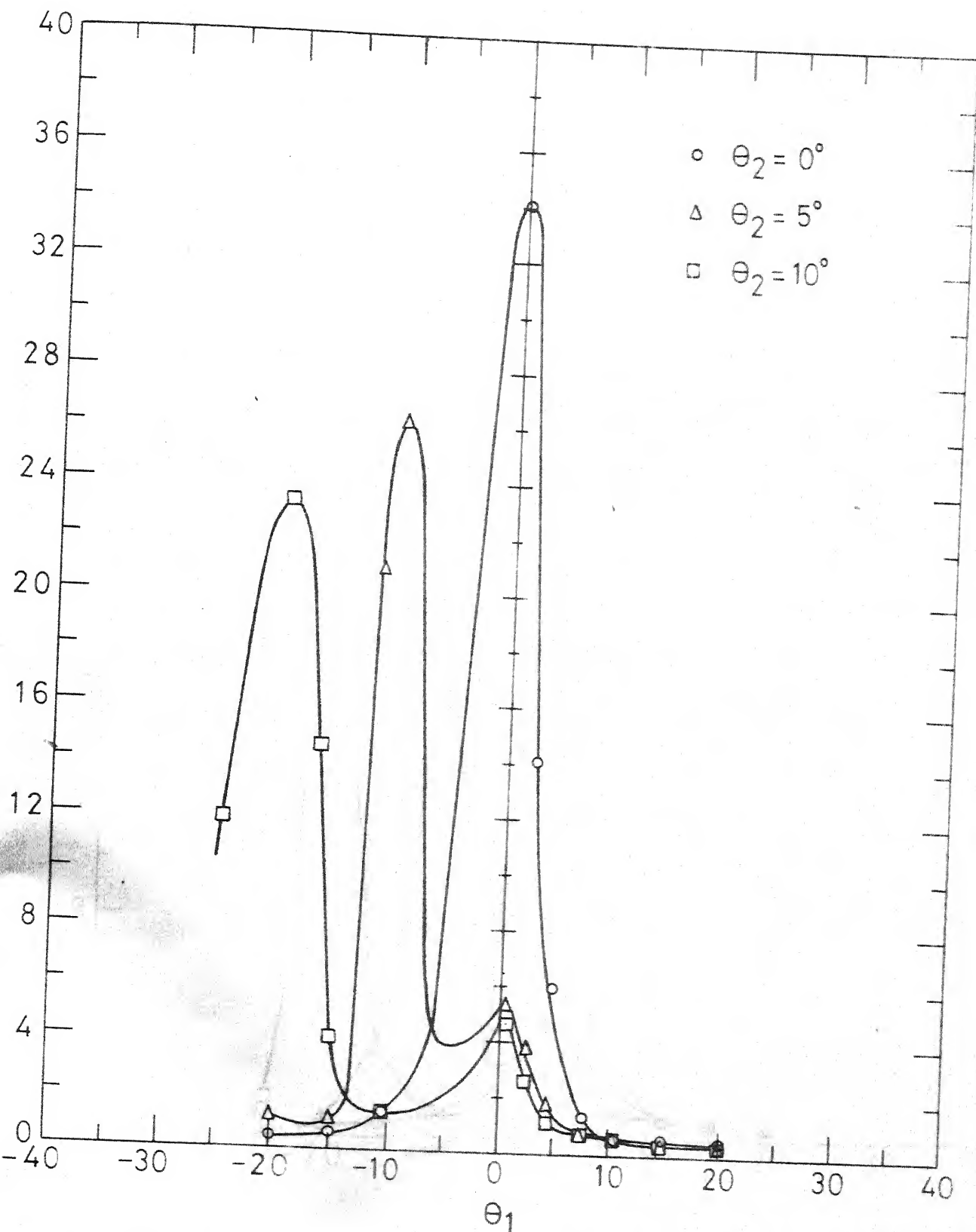




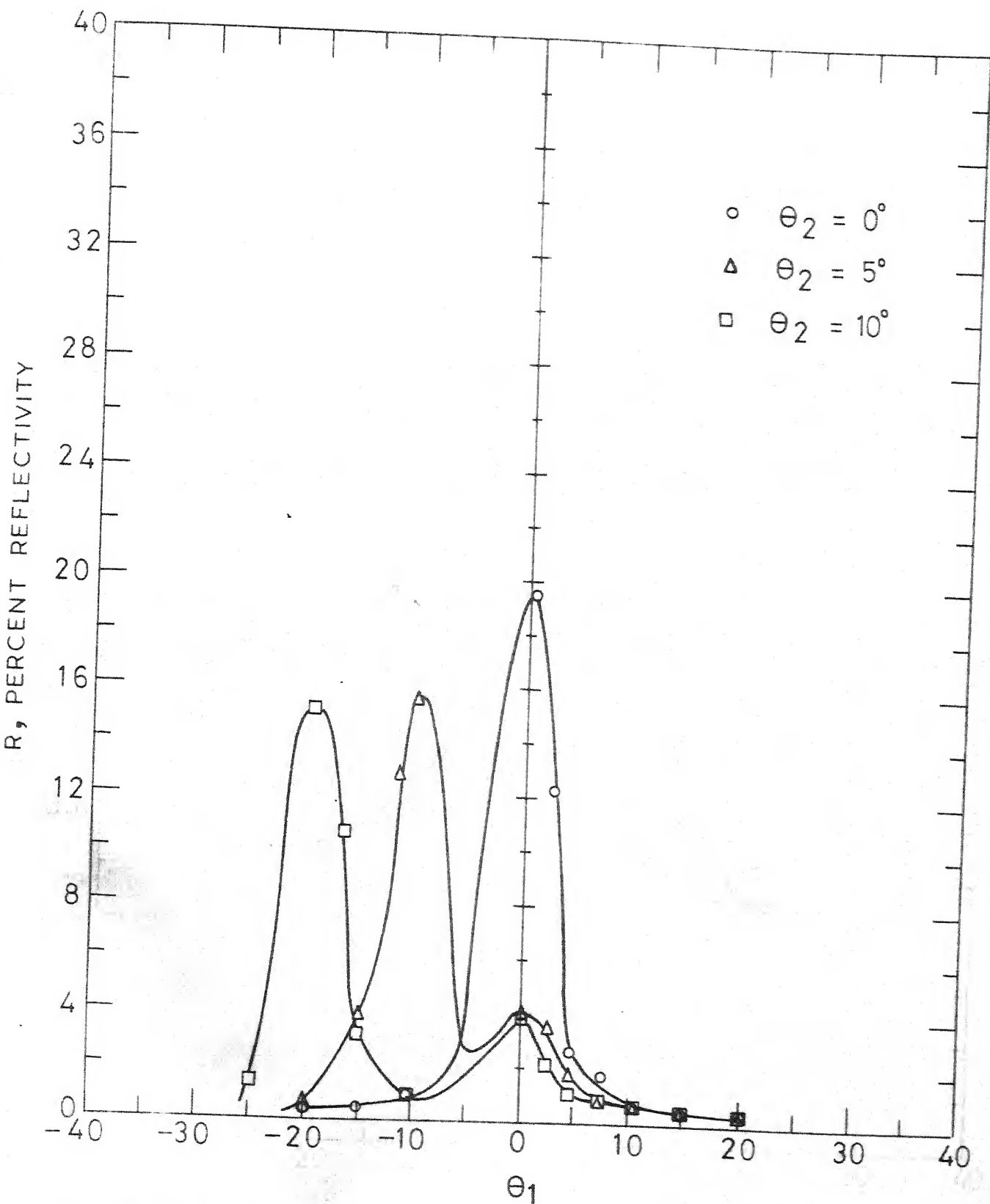
G. 6 CUMULATIVE PLOT OF NUMBER SIZE DISTRIBUTION FOR UNSPHEROIDISED GLASS PARTICLES



CUMULATIVE PLOT OF NUMBER SIZE DISTRIBUTION FOR GLASS SPHERES USED FOR COATING ON SURFACES FOR THE STUDY OF THEIR REFLEX-REFLECTIVE CHARACTERISTICS



8 REFLEX-REFLECTIVE CHARACTERISTICS OF 22 MICRON GLASS SPHERES COATED ON A BUFFED ALUMINUM SURFACE



9 REFLEX-REFLECTIVE CHARACTERISTICS OF 52 MICRON GLASS SPHERES COATED ON A BUFFED ALUMINUM SURFACE

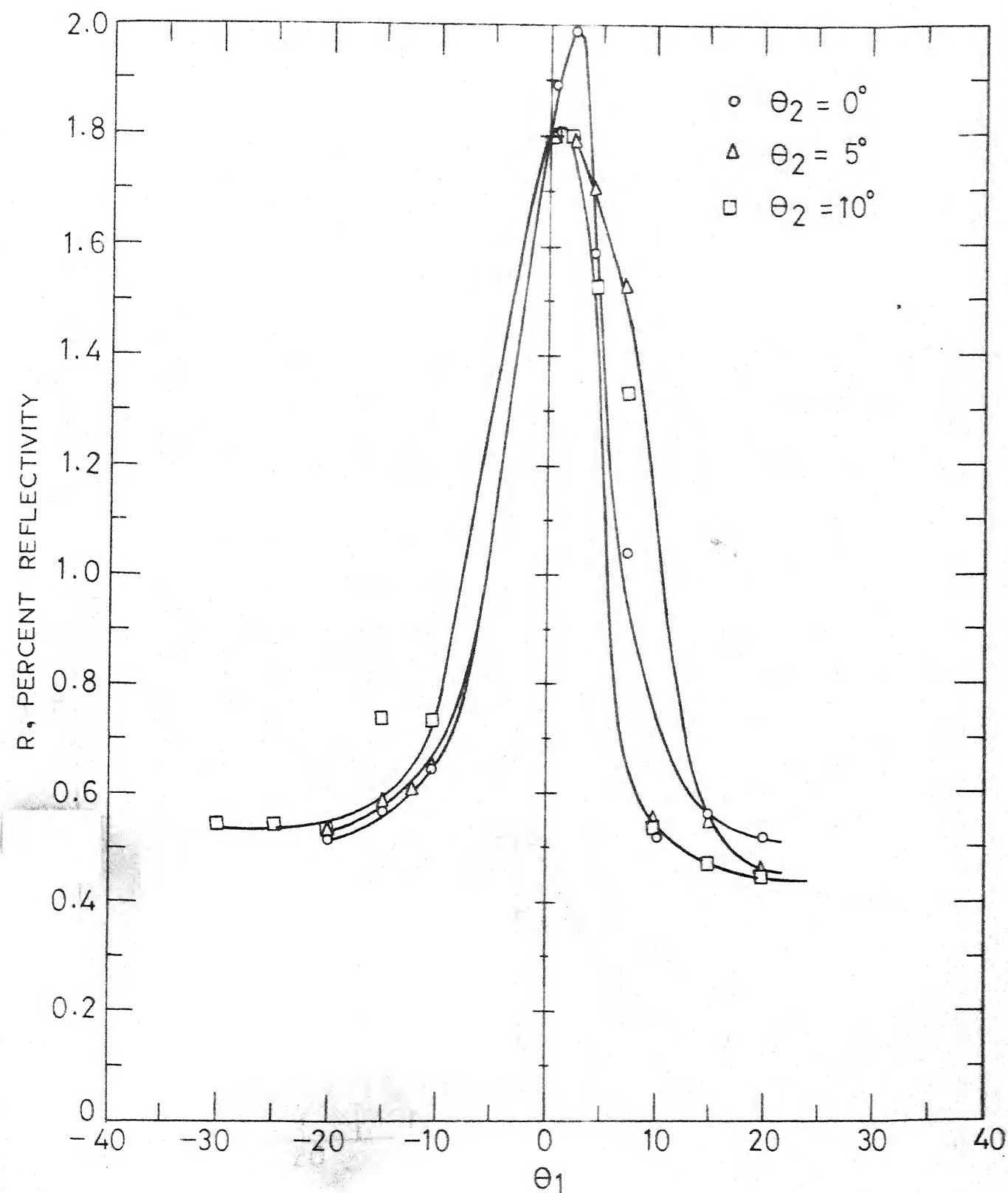


FIG. 10 REFLEX-REFLECTIVE CHARACTERISTICS OF 22 MICRON GLASS SPHERES COATED ON NONREFLECTING BLACK PAPER

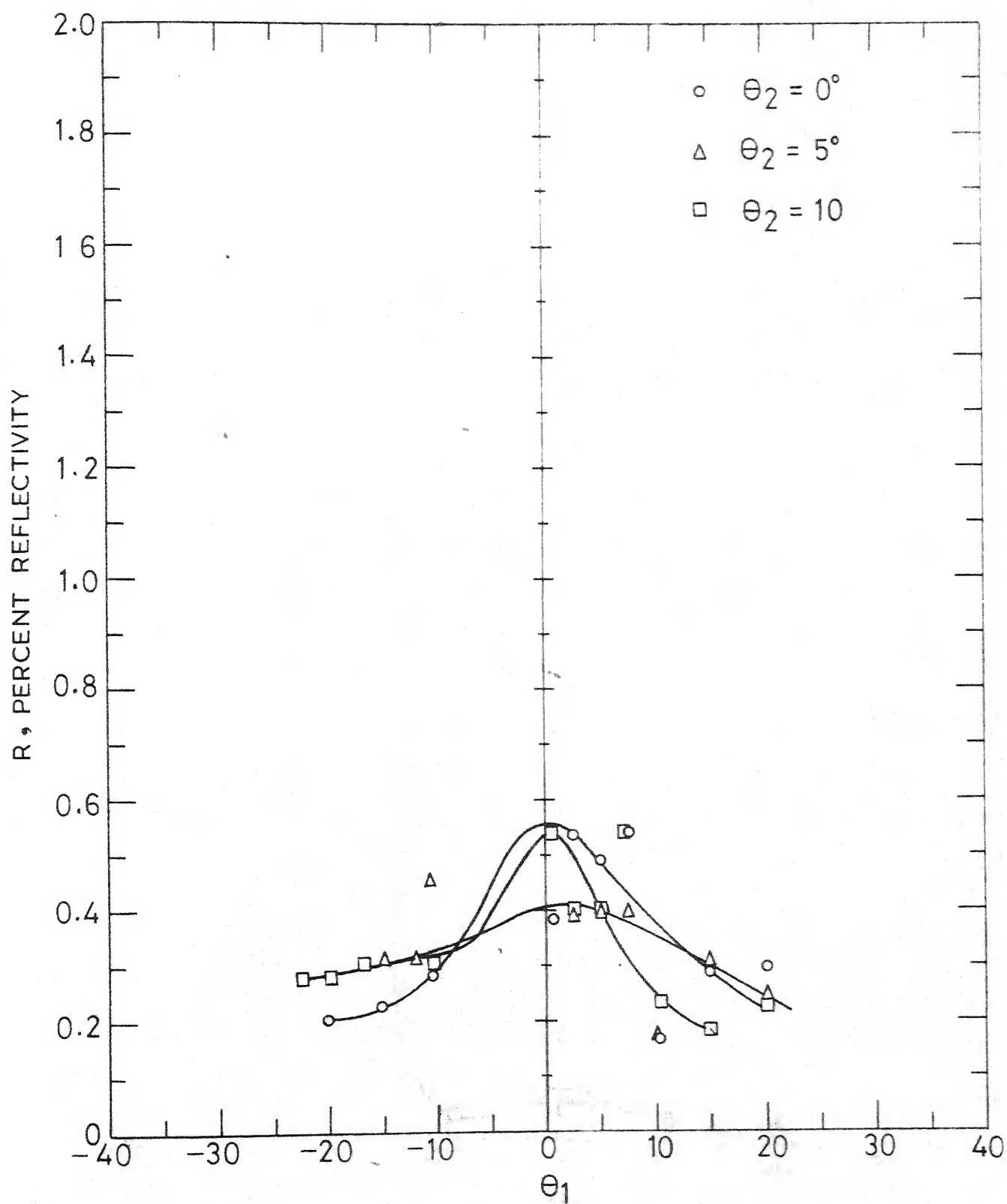


FIG.11 REFLEX-REFLECTIVE CHARACTERISTICS OF 52 MICRON GLASS SPHERES COATED ON NON REFLECTING BLACK PAPER



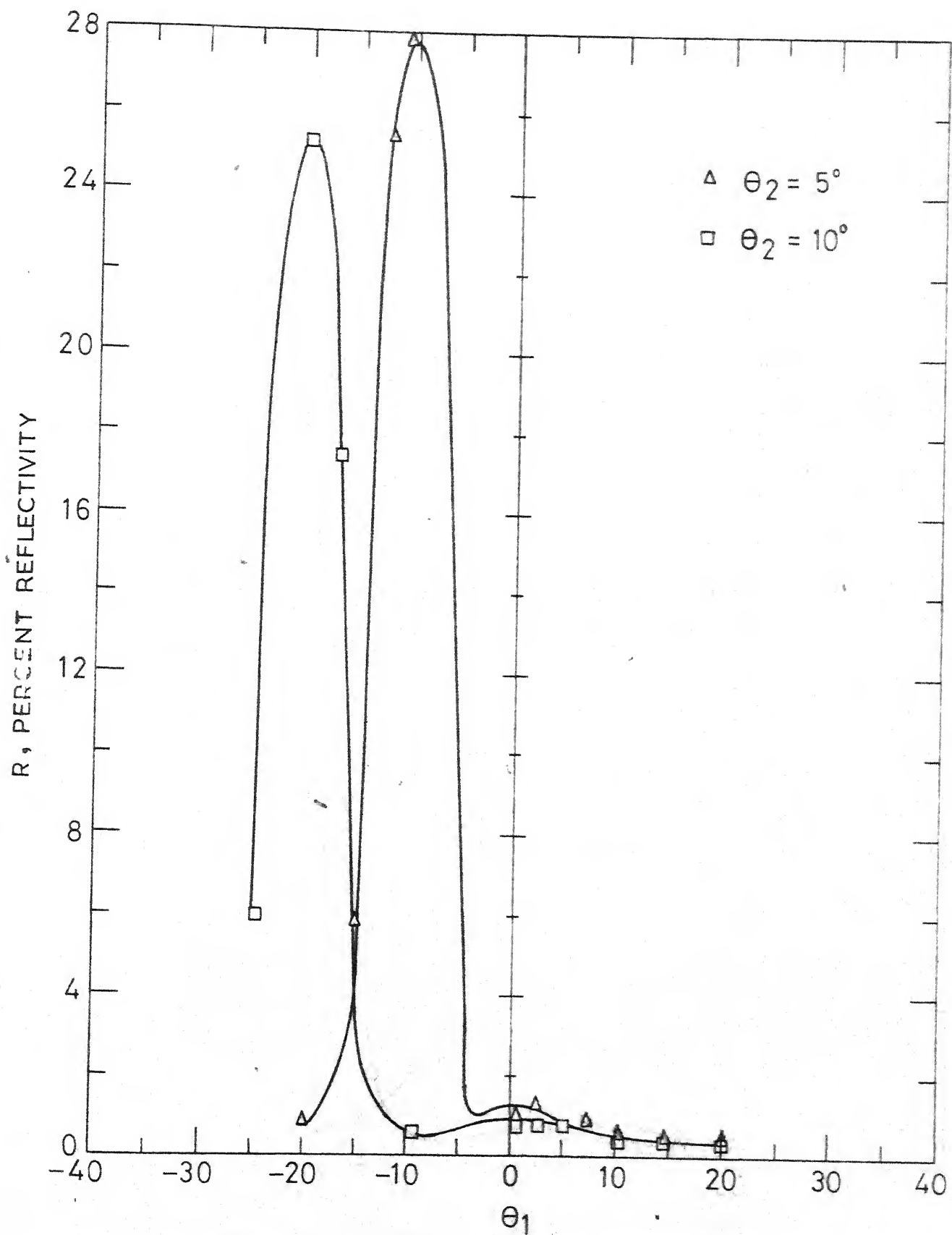


FIG.12 - REFLEX-REFLECTIVE CHARACTERISTICS OF 52MICRON GLASS SPHERES COATED ON A MIRROR

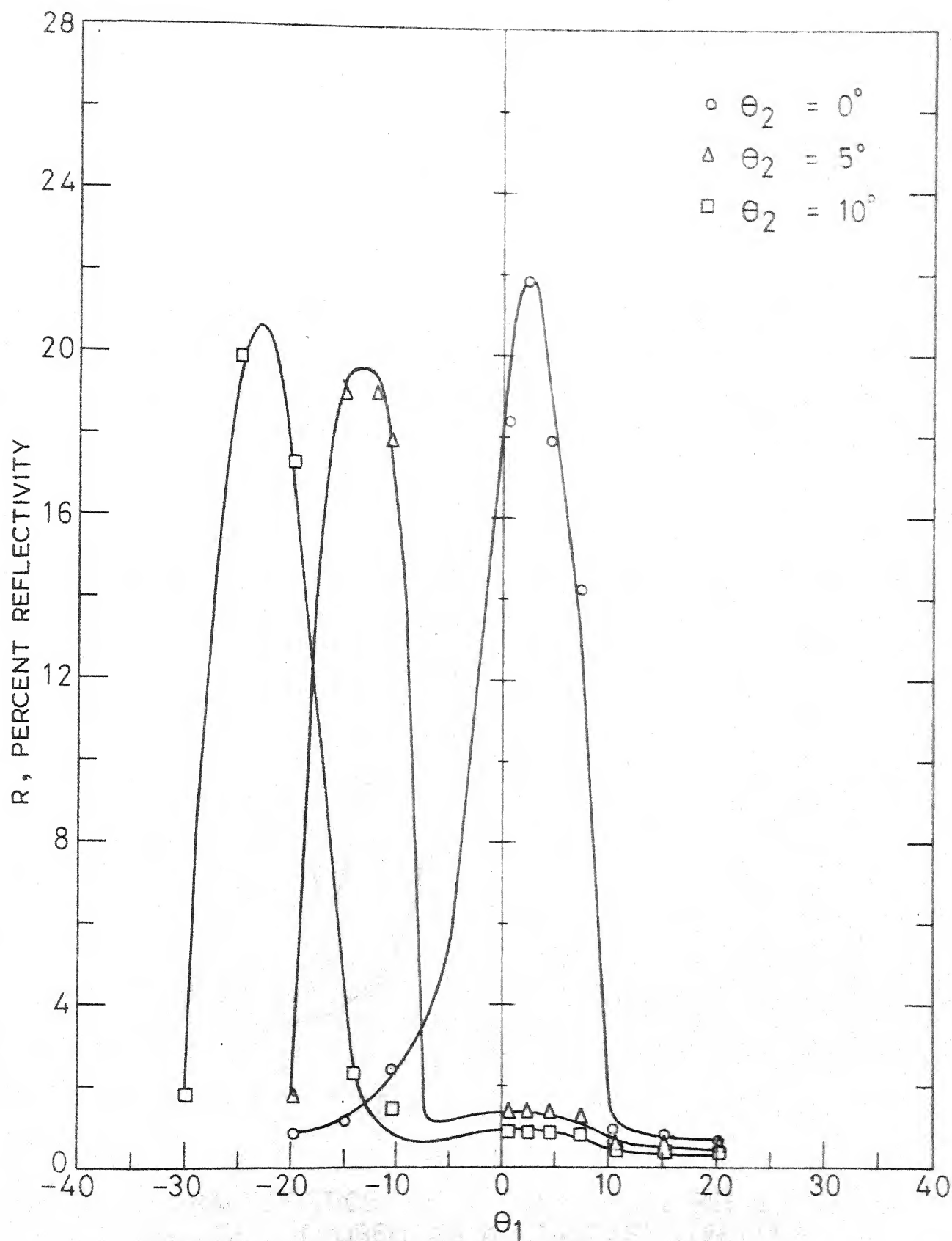


FIG. 13. REFLEX-REFLECTIVE CHARACTERISTICS OF 22 MICRON GLASS SPHERES COATED ON A MIRROR

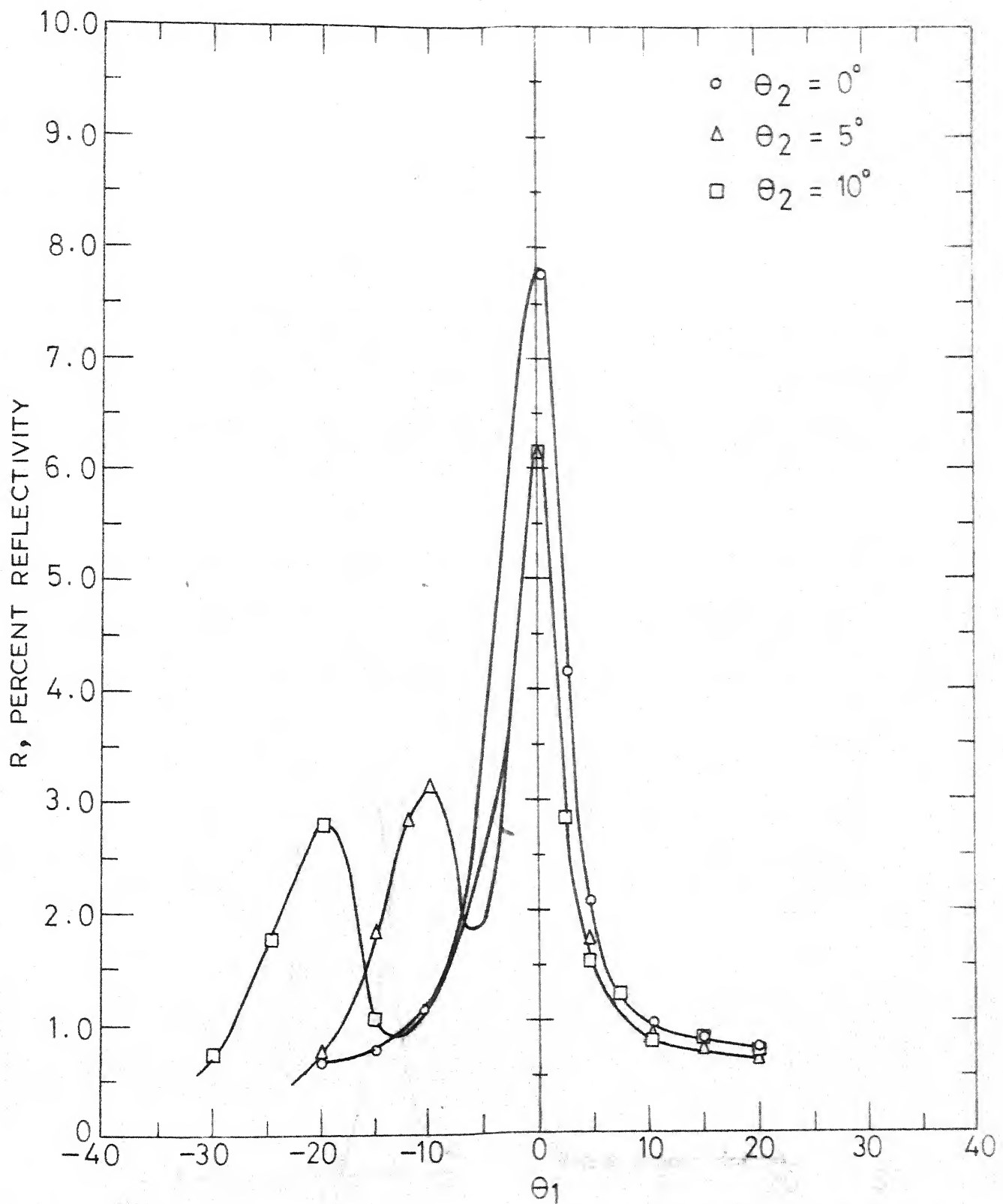


FIG. 14 CHARACTERISTICS OF A COMMERCIAL REFLEX-REFLECTING SHEET USED AS A STANDARD FOR COMPARING BEHAVIOUR OF SURFACES COATED WITH 52 AND 22 MICRON GLASS SPHERES.

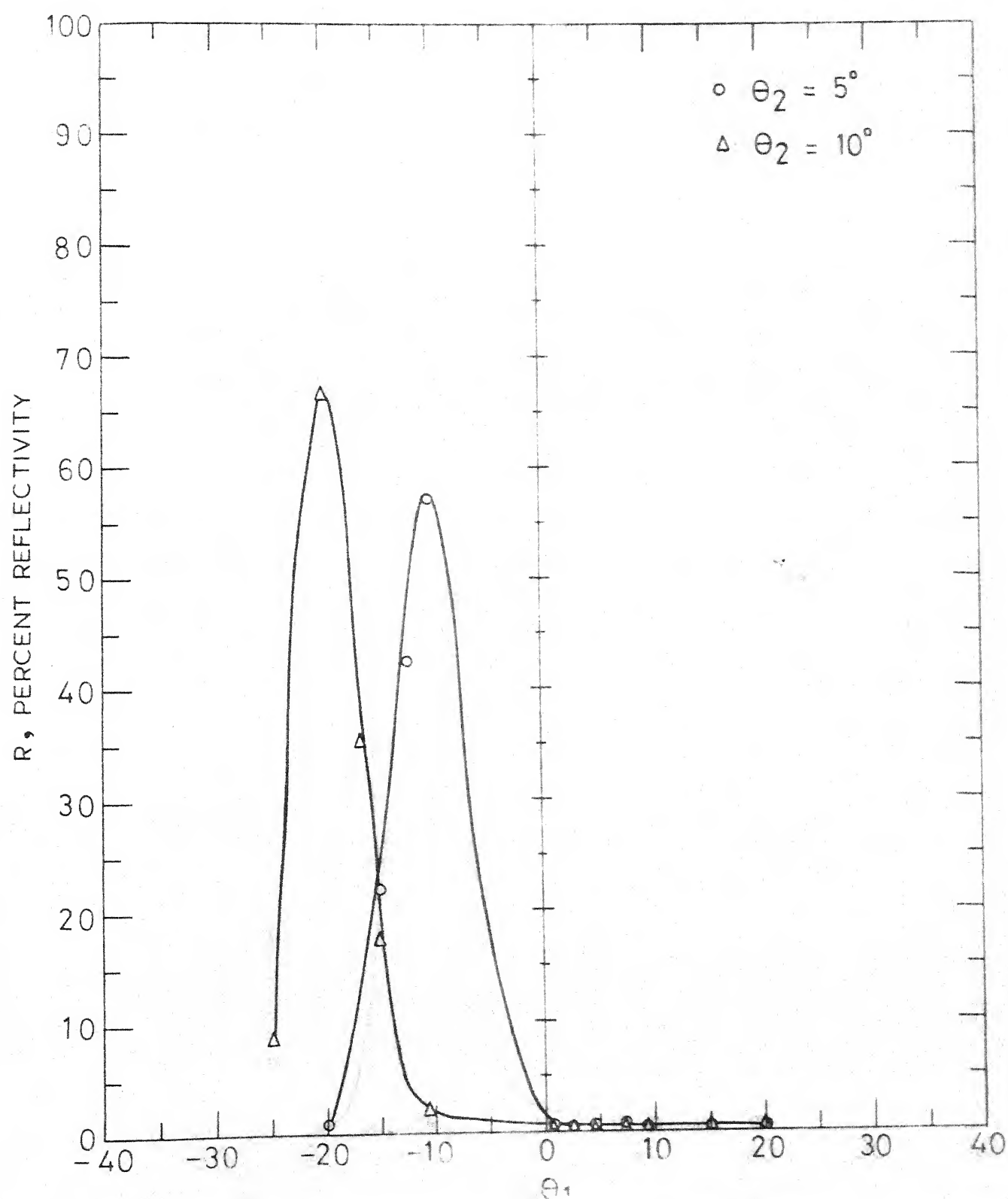


FIG.15 REFLECTING CHARACTERISTICS OF THE BUFFED ALUMINUM SURFACE USED AS A BACKING SURFACE IN THE STUDY OF REFLEX-REFLECTIVE CHARACTERISTICS OF GLASS SPHERES

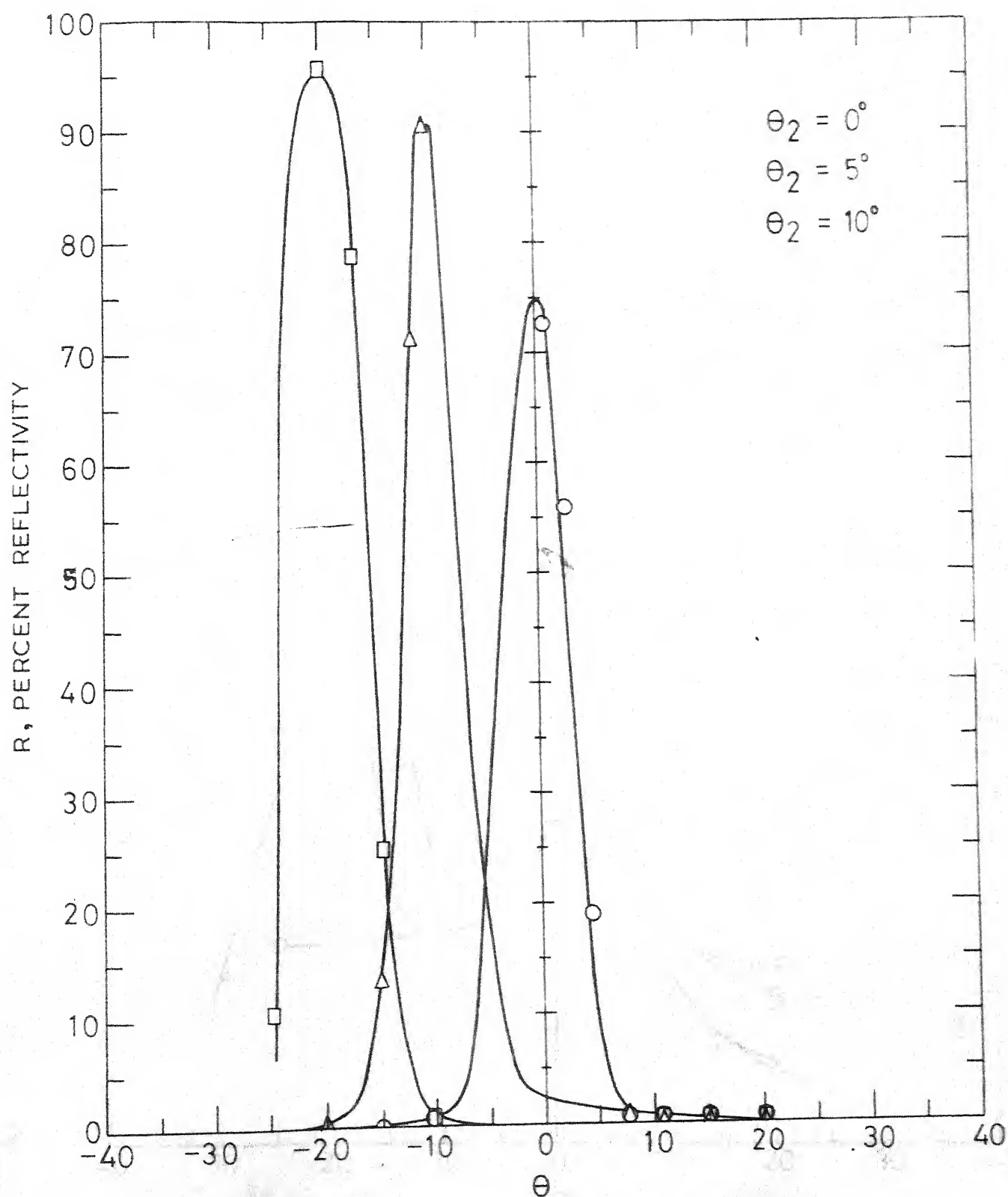


FIG. 16 REFLECTING CHARACTERISTICS OF THE MIRROR USED AS BACKING SURFACE IN THE STUDY OF REFLEX-REFLECTIVE CHARACTERISTICS OF GLASS SPHERES.

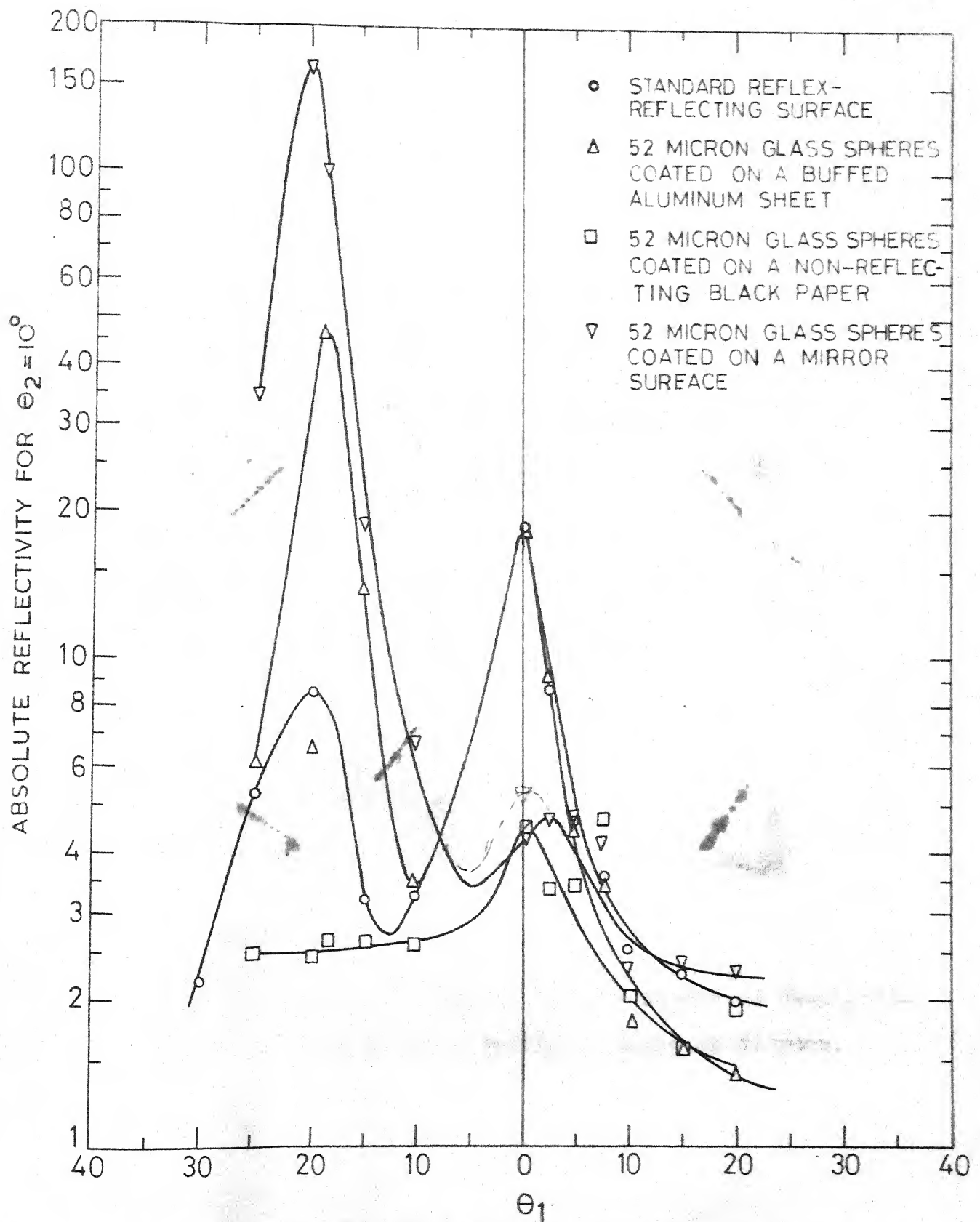
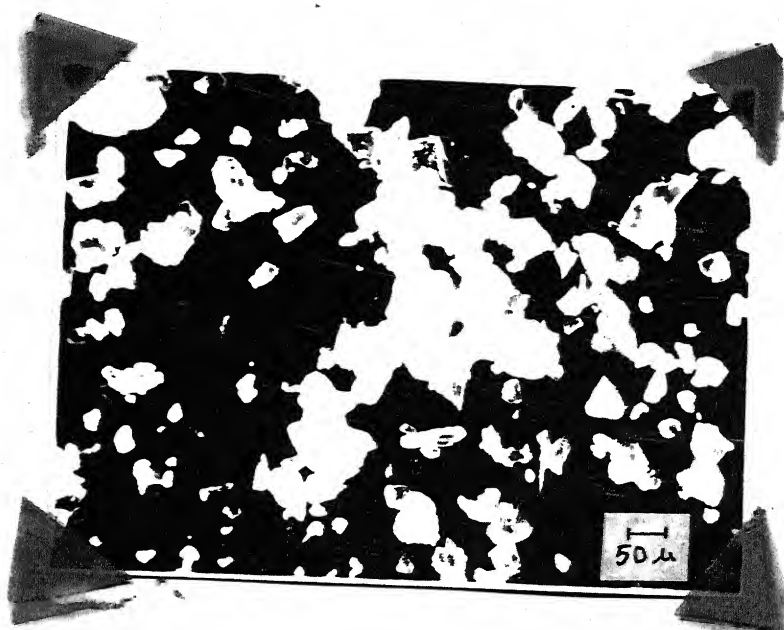
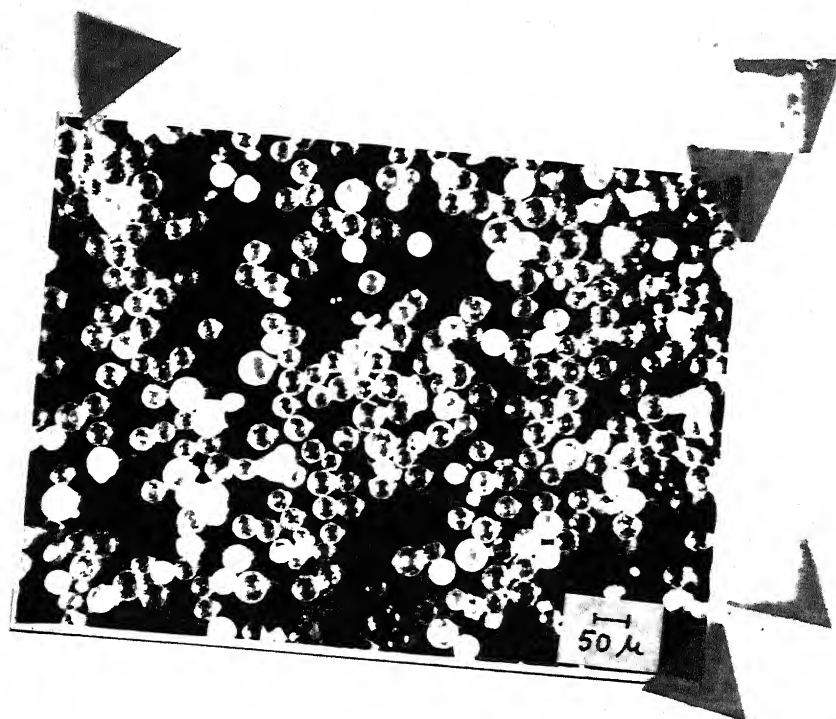


FIG.17 REFLEX-REFLECTIVE CHARACTERISTICS OF SURFACES COATED WITH 52 MICRON GLASS SPHERES.

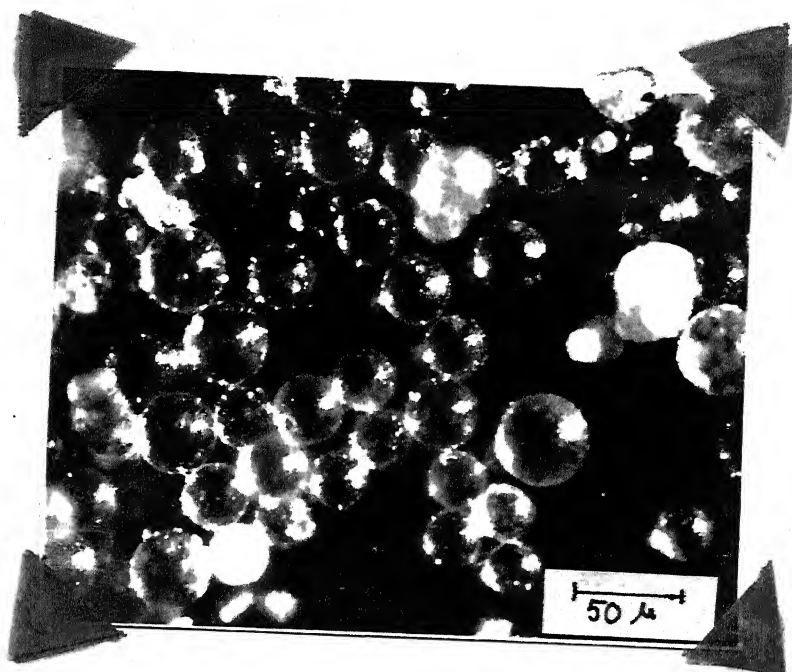




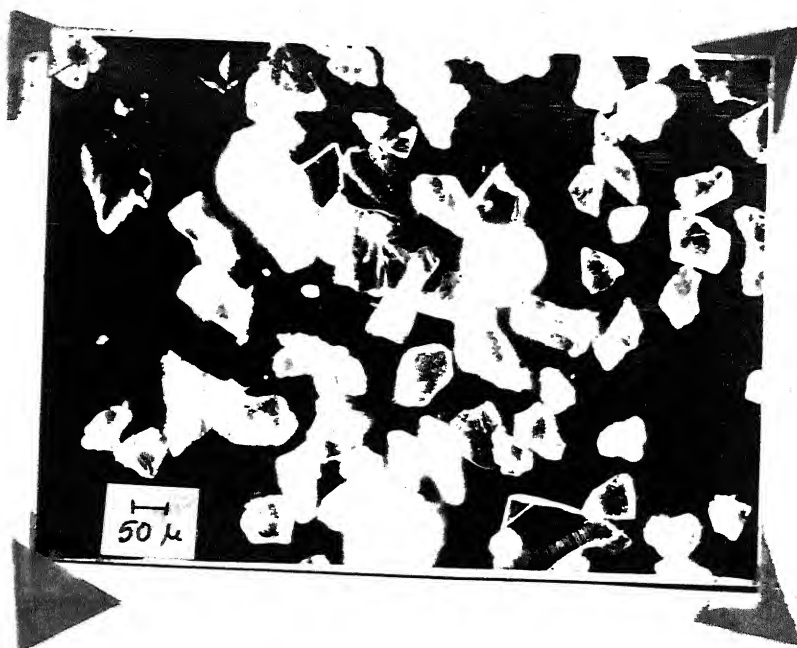
Picture 1: Representative Photomicrograph of Unspherulized Glass Particles below 40 Microns.



Picture 2: Representative Photomicrograph of  
22 Micron Glass Spheres.



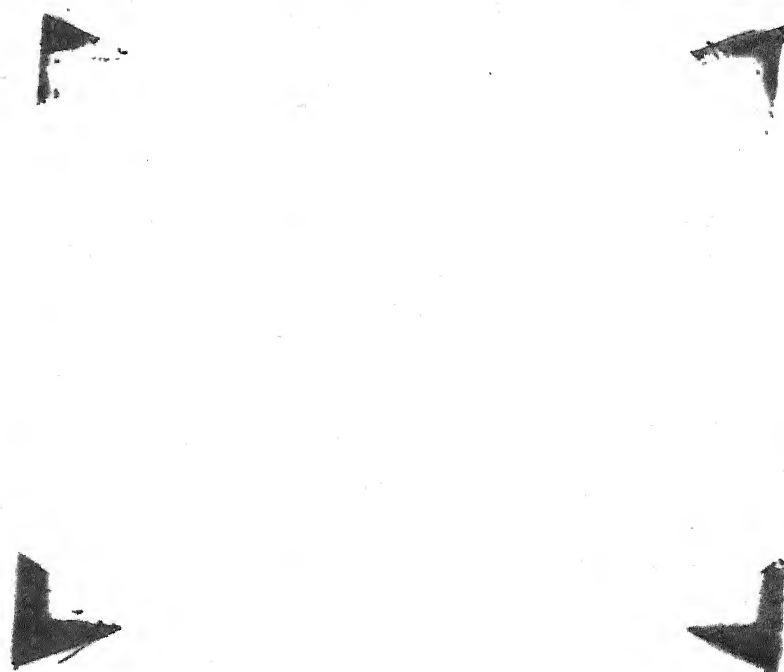
Picture 3: Photomicrograph Showing Bubbles in  
22 Micron Glass Spheres.



Picture 4: Representative Photomicrograph of Un-spheroidised Glass Particles above 40 Microns.



Picture 5: Representative Photomicrograph of  
52 Micron Glass Spheres.



Picture 6: Photomicrograph Showing Bubbles in  
52 Micron Glass Spheres.

## APPENDIX B

### Illustration of the Method Used in the Calculation of Percent Reflectivity:

Referring to the arrangement shown in Fig. 4, if A is the area of the specimen exposed to incident beam of light, then,

$$\begin{aligned} \text{Area of specimen normal to the incident beam of light} \\ = A \cos \theta_2 \end{aligned}$$

where,  $\theta_2$  is the angle between normal to the specimen and axis of the incident beam of light.

Area of specimen normal to the reflected beam of light received on the photocell

$$= A \cos |\theta_1 + \theta_2|$$

where,  $\theta_1$  is the angle between the normal to the photocell, coinciding with the reflected light beam, and the axis of the incident beam of light. It can take negative values on the other side of the axis of incident beam.

If  $I_0$  and I are the intensities of the incident beam of light and reflected beam of light respectively, then percent reflectivity can be defined as,

$$\text{Percent Reflectivity, } R = \frac{\text{(Amount of Reflected light from unit area of the specimen)}}{\text{(Amount of light incident on unit area of the photocell)}} \times 100$$

---

\* Area on the photocell is taken to be same as A on the specimen.



$$= \frac{I/(A \cos |\theta_1 + \theta_2|)}{I_0/(A \cos \theta_2)} \times 100 = \frac{I}{I_0} \times \frac{\cos \theta_2}{\cos |\theta_1 + \theta_2|} \times 100$$

I was recorded with the photocell at angle  $\theta_1$  from the axis of the incident beam of light and  $I_0$  was recorded with photocell on the axis of the incident beam at a point  $\theta_1 = 180^\circ$ . I and  $I_0$  both were read across a standard, precision, resistor on a microvoltmeter to which the photocell was connected.